PB 180504

Behavior of
Surfactants and Other Detergent Components in Water and Soil-Water Environments

A REPORT OF A
COOPERATIVE RESEARCH PROJECT BETWEEN THE
FEDERAL HOUSING ADMINISTRATION
TECHNICAL STUDIES PROGRAM AND THE
UNITED STATES GEOLOGICAL SURVEY
WATER RESOURCES DIVISION

A TECHNICAL STUDIES PUBLICATION
FEDERAL HOUSING ADMINISTRATION
A CONSTITUENT OF HOUSING AND HOME FINANCE AGENCY
WASHINGTON, D. C. 20411

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BEHAVIOR OF SURFACTANTS AND OTHER DETERGENT COMPONENTS IN WATER AND SOIL-WATER ENVIRONMENTS

A Report Prepared
for the
Technical Studies Program
of the
Federal Housing Administration

by
Cooper Wayman,
H. L. Page,
and
J. B. Robertson
Water Resources Division
United States Geological Survey
Washington, D. C.

This does not constitute a revision of FHA standards.

FOREWORD

The Federal Housing Administration is concerned with the livability of the properties for which it issues mortgage insurance. Through the Technical Studies Program, FHA sponsors research which is directed toward better housing and better living. Publication of the technical information in this bulletin is a part of our effort to attain this goal.

Philip N. Brownstein

Philip N. Brownstein
Commissioner

PREFACE

This publication about detergents in ground water is the final report of a cooperative research project between the Federal Housing Administration and the United States Geological Survey.

Synthetic detergents do not occur naturally in ground water, and their presence is an indication of sewage pollution. Unlike other organic wastes, alkylbenzenesulfonate (ABS) is not readily broken down by microorganisms. It moves with the sewage effluent, often into the ground water. ABS can be detected in low concentrations and thus used to trace sewage pollution. In relatively high concentrations, it will cause noticeable foaming, taste and odor nuisances, all of which are objectionable. The problem is most serious in areas where individual sewage disposal systems and individual wells are widely used and the subsoil is permeable. This permits sewage effluent to be drawn into the water supply and is of concern to health authorities and homeowners.

Although the Federal Housing Administration requires central water and sewerage systems wherever feasible, there are some areas where individual systems must be used. FHA engineers and others need to know the characteristics of detergent movement below the ground surface to determine the proper placement of these individual facilities to assure a wholesome water supply. Little information about detergent absorption and degradation has been available to aid in these engineering decisions.

Because detergent pollution has continued to increase, in 1959, FHA's sanitary engineers requested a study of this problem under the Technical Studies Program. FHA contracted with the United States Geological Survey to investigate the magnitude of the problem. Widespread detergent pollution was indicated. Shortly afterward, the FHA-U.S.G.S. research project was initiated.

This publication is concerned mainly with alkylbenzenesulfonate (ABS), the anionic surface-active agent most frequently found in water supplies. The authors discuss the prevalence of ABS as a pollutant, the analytical techniques for determining it, and the way ABS affects certain physical and chemical properties of water. The report gives a good technical basis for understanding the mechanisms and physical principles of detergent movement below the ground surface. It provides an understanding and basis for engineering analysis.

This publication does not constitute an FHA standard.

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INTRODUCTION

In 1960, the estimate of water utilized in the United States was 300 billion gallons per day (bgd). Of this amount about 60 bdg comes from ground water resources, which supplies 90 million inhabitants. By 1980 the amount of water required has been estimated to be twice the above figure. It is apparent that the quality of surface-water and ground-water should be of paramount importance to the development of water supplies from such sources.

Since World War II, scientific progress has produced over 500,000 man-made products for both industrial and household usage. To this vast number, over 50,000 new products are added annually. A significant amount of these compounds are discharged into surface-water or ground-water from industrial effluent water, sewage waste water, cesspools, and septic tanks. Unless these compounds can be chemically degraded (by dissolution of hydrolysis) or oxidized by aerobic bacteria, potential pollution of ground-water or surface-water may be created.

Branched-chain anionic surfactants in synthetic detergents seem to resist significant amounts of normal oxidation or biochemical degradation in water. Thus, when sewage effluents containing these refractory substances are discharged into rivers or streams, pollution of surface-water may occur and pollution of ground-water might result from natural infiltration. Likewise, septic tank or cesspool effluents containing surfactants may pollute ground-water unless removed by soils during infiltration.

The production of surfactants has continually increased by an annual average rate of 90 million pounds. The estimate for annual production by 1965 is two billion pounds (McCutcheon, 1962). The details of surfactant production between 1956 and 1960 are listed in Table 1 (McCutcheon, 1962).

In 1962, the Soap and Detergent association reported that synthetic detergent sales amounted to 3.75 billion pounds or 78 percent of the total soap and detergent market (Chemical and Engineering News, 1963). It is obvious from Tables 1 and 2 that the production and use of surfactants has not reached its plateau. Considering increase of population, the annual per capita use of synthetic detergents has increased from 19 pounds (1948) to 24 pounds (1960). Unless better biodegradable surfactants are produced, such materials will increase the so-called "detergent" pollution of water supplies in the future.

Synthetic detergents are composed essentially of two ingredients, organic surface active agents (surfactants) and inorganic phosphate builders. These formulations also contain minor amounts of perfumes, optical bleaches, inorganic sulfate, silicate, and carboxymethylcellulose. Surfactants are essential to detergency because of the property of lowering of surface tension, so necessary in wetting, dispersion, emulsification, and hardness stability. Builders are usually added to compliment the properties of surfactants or as diluents. The water-soluble surfactants employed in synthetic detergents comprise four different types:

(1) Amphoteric - which ionise in solution with either a positive or negative charge on the long-chain ion dependent upon pH. An example of this surfactant is the long chain amino acids (Osipow, 1962) which is cationic in acid solution and anionic in basic solution.

Table 1.—*Production of surfactants as 100 percent active material, in thousands of pounds*

Year	1956	1957	1958	1959	1960
Anionic	872,000	901,000	976,622	1,067,560	1,074,213
Nonionic	257,000	285,000	341,942	400,424	426,246
Cationic and Amphoteric	19,000+	20,000++	34,510	36,075	31,768
Total	1,148,006	1,206,000	1,355,074	1,504,059	1,532,227

+ Cationic only
++ Cationic only, and prorated from 1956 production
Data from U. S. Tariff Commission Reports.

Table 2.—*Total soap and synthetic detergent sales, in thousands of pounds*

Year	Soap	Synthetic detergents	Total	1948=100	Percent total round numbers represented by synthetic detergents
1948	2,517,790	401,863	2,919,653	100	14
1949	2,488,336	712,456	3,200,792	110	22
1950	2,484,931	1,093,188	3,578,119	122	31
1951	2,057,524	1,255,246	3,312,770	113	38
1952	1,870,104	1,530,119	3,400,223	116	45
1953	1,645,431	1,866,883	3,512,314	120	53
1954	1,443,313	2,063,276	3,506,589	120	59
1955	1,350,464	2,317,478	3,667,942	126	63
1956	1,285,112	2,690,327	3,975,439	136	68
1957	1,188,909	2,915,766	4,194,675	141	71
1958	1,138,148	2,951,352	4,089,500	140	72
1959	1,066,440	3,203,437	4,269,877	146	75
1960	1,056,936	3,310,650	4,367,586	150	76

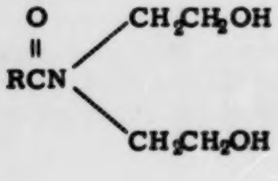
Data from Association of American Soap and Glycerine Producers, Incorporated.

$$RNHCH_2COOH \xrightarrow{HCl} (RNH_2CH_2COOH)^+Cl^- \text{ (acid)} \quad (1)$$

where R is the long-chain alkyl group

$$RNHCH_2COOH \xrightarrow{NaOH} (RNHCH_2COO)^-Na^+ \text{ (basic)} \quad (2)$$

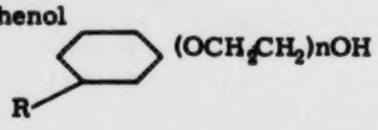
(2) Nonionic - which do not ionize in solution. There are various types of nonionics such as the fatty alkanolamide (Kritchevsky, 1937) as represented by



(3)

By far the most diverse group is derived from ethylene oxide such as (Osipow, 1962)

alkylphenol

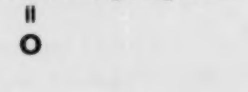


(4)

fatty alcohol

$$R(OCH_2CH_2)nOH \quad (5)$$

fatty acid



$$RC(=O)(OCH_2CH_2)nOH$$

(6)

fatty mercaptan

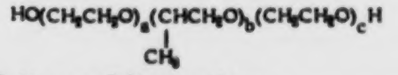
$$RSCH_2CH(OCH_2CH_2)nOH \qquad (7)$$

fatty amine

$$R(R^1)NCH_2CH_2(OCH_2CH_2)nOH \qquad (8)$$

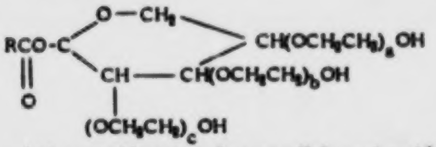
R^1 is the short-chain alkyl group

polyoxypropylene glycol



$$HO(CH_2CH_2O)_a(\underset{\substack{|\\CH_3}}{CH}CH_2O)_b(CH_2CH_2O)_cH \qquad (9)$$

fatty sorbitan esters



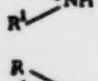
(10)

One interesting and possibly significant group of nonionic surfactants is the so-called sugar-base surfactants. These sugar esters are prepared from an alcoholysis reaction of a methyl ester of fatty acid with sucrose employing potassium carbonate as a catalyst. It has been indicated that only the mono-fatty-acid esters of the C_{12} to C_{18} group are soluble in water (Osipow, 1962). These surfactants might possess a possible solution to the pollution problem. Recently, it was reported (Chemical and Engineering News, 1963, p.55) that certain sugar esters of hydrozy fatty acids can be made totally biologically degradable with additional attractive properties of low-foaming, relatively cheap production, and lack of toxicity.

(3) Cationic - which ionize in solution with a positive charge on the long-chain ion. These surfactants consist of two groups, amines and quaternary ammonium compounds. The long-chain primary, secondary, and tertiary amines are water soluble in acid solution. The ethozylated amines are soluble over a wide range of pH but carry a positive charge only in acid solution. Examples of the amine group are (Osipow, 1962):

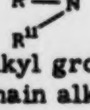
primary amine $R—NH_2$ (11)

secondary amine



(12)

tertiary amine



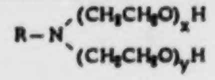
(13)

R is a long-chain alkyl group
R^1, R^{11} are short-chain alkyl groups

diamine

$$R—NHCH_2CH_2CH_2NH_2 \qquad (14)$$

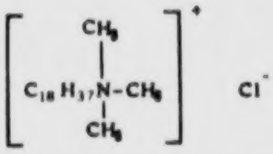
polyethozylated amine



(15)

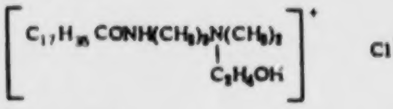
The quaternary ammonium compounds can be represented as:

aquad 18-50



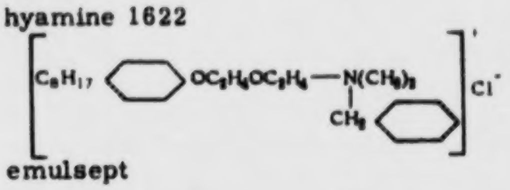
$$\left[C_{18}H_{37}\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{N}}-CH_3\right]^+ Cl^- \qquad (16)$$

aerosol SE



$$\left[C_{17}H_{35}CONH(CH_2)_3\underset{\substack{|\\C_2H_4OH}}{N}(CH_3)_2\right]^+ Cl^- \qquad (17)$$

hyamine 1622



(18)

emulsept

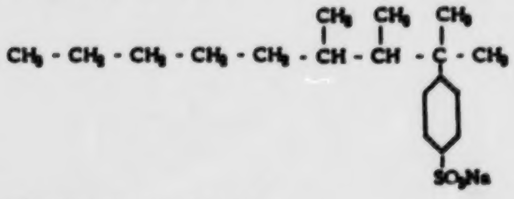
$$[C_{11}H_{23}COOC_2H_4NHCOCH_2N(CH_3)_3]^+ \; Cl^- \qquad (19)$$

(4) Anionic - which ionize with a negative charge on the long-chain ion. These surfactants, specifically the sulfonates, are the most important with respect to water pollution by virtue of the amount produced (Tables 1 and 2) and because of their inability to be completely bio-degradable. Sulfonates are excellent synthetic detergents because of their detergency properties and because they do not form precipitates with calcium or magnesium salts in hard water. These anionics are usually produced as sodium salts of dodecylbenzene sulfonate or propylenetetramer benzene sulfonate. The manufacturing process consists essentially of the following (Osipow, 1962):

Alkylbenzene is made by polymerization of propylene and subsequently consensed with benzene employing hydrogen fluoride or aluminum chloride as condensing agents. This alkylate is a branched chain mixture with 10 to 15 carbon atoms in the alkyl with average molecular weight of 246. The alkylate is sulfonated with oleum or sulfur trioxide and neutralized to produce the sodium salt of alkylbenzenesulfonate in combination with sodium sulfate. The composition of commercially packaged anionic detergents such as "Tide" and "Fab" is quite variable but most likely could be represented by

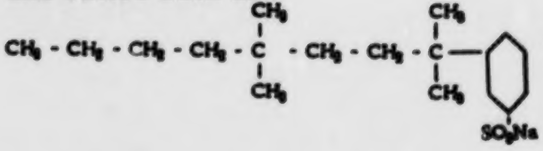
organic surfactant	10 to 40 percent
sodium tripolyphosphate	25 to 50 percent
sodium sulfate	5 to 10 percent
sodium carboxymethylcellulose	1 percent
sodium silicate	2 to 10 percent
optical bleach	trace

Laundering concentrations usually contain 200 to 600 parts per million (ppm) of surfactant. Optimum detergency occurs at about pH 10 to 11 and can be controlled by phosphate, carbonate, or silicate. Phosphates and silicates also function as water softeners and suspending agents. Carboxymethylcellulose usually acts to prevent soil redeposition. The structures of significance to water pollution are quite variable and can be classified as either "hard" or "soft" surfactants. The anionic surfactants presently used in synthetic detergents ("hard") are complexly branched-chained with limited bio-degradation (50 to 65 percent in sewage) and represented by the structure (Continental Oil Company, 1955):

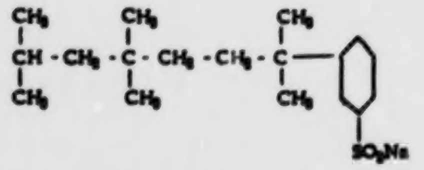


(20)

and others such as

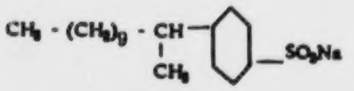


(21)



(22)

At the present time much effort has been devoted to newer types of anionic surfactants ("soft") containing essentially a straight-chain configuration and being about 85 to 90 percent biodegradable by sewage with typical structures such as



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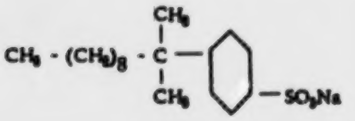

(24)

For reasons of simplicity and emphasis in this report, anionic surfactants ("hard") will receive the bulk of consideration because of their importance to water pollution studies and will be referred to as ABS with typical structures (20), (21), and (22) unless otherwise indicated.

The types of water problems arising from incompletely degradable surfactants in detergents have been summarized in a recent report (Soap and Detergent Association, 1962):

(1) The appearance of foam on some surface waters — particularly on streams and rivers that receive untreated sewage, or the effluent of sewage treatment plants.

(2) The appearance of a slight transient foam and measurable levels of ABS in water from private wells, generally in areas in which household wastes are being handled in nearby septic tanks. Also, allegations of "detergent" taste and odors in well water.

(3) Increased foaming at the sewage treatment plants —along with the expressed belief on the part of some operators that plant efficiency is being lowered.

(4) The presence of ABS in public water supplies.

(5) The effect of minute amounts of ABS on micro-organisms, fish, and plant life.

(6) The possibility of a continuous build-up of ABS in municipal wells and other water supplies.

(7) Septic tank troubles ascribed arbitrarily to the use of detergents.

(8) Difficulties observed in some apartment-house waste water systems (suds back-up).

(9) The problems of disposing of untreated

laundry waste water in areas not served by public sewer systems.

In addition to the above effects of surfactants, it is essential to determine whether ABS or other surfactants are toxic to humans if ingested at low concentrations (0.01 to 0.001 ppm) for long periods of time (several to several tens of years). There are many speculative aspects of carcinogenosis with respect to surfactants as indicated recently (Hueper, 1960):

> "Detergents when in contact with the mucosa of the alimentary tract may facilitate and accentuate the contact of the mucosa with carcinogens (cancerous substances) of various types ingested with food and may simultaneously increase the permeability of the mucosa cells to these extraneous carcinogens, thereby activating or aggravating their carcinogenic effect upon these tissues or their transport and their action on remote tissues. Observations made with the experimental use of detergents administered by mouth in combination with polycyclic aromatic carcinogens to mice support the occurrence of this role of detergents in chemical carcinogenesis. Another aspect is related to the cocarcinogenic properties possessed either by the dodecylbenzol mixture itself from which by sulfonation the detergent dodecylbenzolsulfonate present in all household detergents is produced or by an impurity, dodecane, sometimes present in this mixture. It is uncertain, however, whether the cocarcinogenic effect of these materials observed on the skin of mice when exposed to a known carcinogen is present also on the alimentary mucosa and whether it exists for tissues of man. Nevertheless, the possibility of such an effect from household and industrial detergents upon the alimentary mucosa cannot be dismissed, especially since dodecylbenzol is a chemically indefinite mixture of alkylbenzol compounds obtained from petroleum, and because other surfactants used in the food industry have shown carcinogenic properties (Tween 60 and Tween 80) or have displayed even carcinogenic qualities (polyozyethylene stearate) when fed to mice and rats, respectively."

Opinions of others indicate that anionic surfactants like ABS are essentially nontoxic. Lehman (1950) suggested that ABS was low enough in toxicity to be used as a detergent for fruits and vegetables. In a study on acute oral toxicity of synthetic detergents, no harmful effects were indicated but long-term studies up to that time were inadequate to establish their safety as food additives (Heyroth, 1954). The present and anticipated concentrations of detergents in rivers and streams are not believed to offer any toxicity from long-term ingestion of water (Smyth, 1955). Studies by the British Government (Report of the Committee on Synthetic Detergents, 1956) and similar reports in the United States (AWWA Task Group 2661-P, 1954 and 1957) imply that no evidence can be found for serious acute toxicity from detergents.

Toxicological studies of ABS on animals indicate that the oral LD_{50} ranges between 1.0 to 2.3 g. per kg. of body weight (Hine, 1953; Hopper and others, 1949; and Woodward and others, 1945). LD_{50} represents the amount of substance per unit body weight required to kill one-half of a group of animals of a given species under specified conditions. Specific studies of short duration relating to oral ingestion of ABS have not indicated any serious degree of toxicity to rats, dogs or humans (Freeman and others, 1945), guinea pigs (Woodward and Calvery, 1945), mice (Hopper and others, 1949), and swine (Beeson and others, 1953; Havermann and Ruter, 1954; and Havermann and Menke, 1959). Though previous studies of short duration have indirectly established no specific toxicity of ABS, this possibility should not be dismissed until data are available to establish that humans or animals having digestive systems similar to humans do not suffer from toxic effects when administered low concentrations of detergents for long periods of time (several years).

The occurrence of ABS in various types of natural or waste water is well documented in the literature. A detailed study of ABS in public water supplies in 32 cities of the United States has been recently reported (Association of American Soap and Glycerine Producers Committee Report, 1961). The results of this study are shown in Table 3, ABS in Public Water Supplies in the United States. The average content of ABS for these samples was 0.024 ppm (parts per million) for a concentration range of 0.00 to 0.14 ppm. The highest and lowest ABS

Table 3.—*ABS in public water supplies in the United States*

City	Approximate population served 1,000's	Water source	Water treatment methods*	Series A		Series B		Series C	
				Sampling month 1959	ABS ppm	Sampling month 1959	ABS ppm	Sampling month 1960	ABS ppm
Albuquerque, N.M.	97	well	1	Aug.	0.04	Nov.	0.02	Mar.	<0.01
Baton Rouge, La.....	126	well	2	Jul.	.02	Nov.	.02	Mar.	.00
Camden, N. J.......	125	well	3	Jun.	.14	Oct.	.02	Mar.	< .01
Janesville, Wis......	25	well	◆	Jul.	.01	Nov.	.00	Mar.	.00
Buffalo, N. Y.......	580	Lake Erie	4	Aug.	.01	Oct.	.02	Mar.	< .01
Chicago, Ill........	3,600	Lake Michigan	5	Jun.	.03	Oct.	< .01	Mar.	< .01
Boulder, Colo.......	20	glacier	◆	Jul.	.01	Oct.	.02	Mar.	< .01
Little Rock, Ark.....	105	alum fork of Saline River	6	Jun.	.00	Nov.	.00	Mar.	.00
New York, N. Y.....	8,100	reservoirs, (Catskill, Croton, Delaware River ‡)	7	Jun.	.00	Oct.	.02	Mar.	< .01
Los Angeles, Calif...	3,560	Colorado River ‡	5	Jul.	.00	Nov.	.02	Mar.	.00
Minneapolis, Minn...	540	Mississippi River ø	8	Jun.	.02	Nov.	.01	Mar.	< .01
Burlington, Iowa	32	Mississippi River ø	8	Jul.	.02	Nov.	.04	Mar.	.02
St. Louis, Mo........	860	Mississippi River ø	9	Jun.	.02	Nov.	.05	Mar.	.04
Vicksburg, Miss......	28	Mississippi River ø	8	Jul.	.03	Nov.	.03	Mar.	< .01
New Orleans, La.....	570	Mississippi River ø	5	Jul.	.02	Nov.	.06	Mar.	< .01
Great Falls, Mont....	44	Missouri River ø	10	Jul.	.00	Dec.	.00	Mar.	< .01
Williston, N. D......	7	Missouri River ø	4	Aug.	.02	Nov.	.00	Mar.	.00
Bismarck, N. D......	20	Missouri River ø	10	Jul.	.01	Nov.	.00	Mar.	.00
Yankton, S. D.......	11	Missouri River ø	4	Aug.	.02	Nov.	.02	Mar.	< .01
Omaha, Neb.........	264	Missouri River ø	6	Jun.	.05	Dec.	< .01	Mar.	< .01
Kansas City, Mo.....	690	Missouri River ø	10	Jun.	.00	Oct.	.02	Mar.	.06
St. Charles, Mo.	15	Missouri River ø	8	Jun.	.02	Dec.	.05	Mar.	.06
East Liverpool, Ohio..	31	Ohio River ø	5	Jun.	.09	Sep.	.04	Apr.	.02
Huntington, W. Va...	120	Ohio River ø	10	Jul.	.06	Nov.	.02	Mar.	< .01
Cincinnati, Ohio.....	634	Ohio River ø	5	Jun.	.03	Oct.	.04	Mar.	.02
Louisville, Ky.......	450	Ohio River ø	5	Jul.	.06	Nov.	.08	Mar.	.03
Paducah, Ky.........	37	Ohio River ø	5	Jun.	.02	Nov.	< .01	Mar.	< .01
Hagerstown, Md.....	30	Potomac River ø	5	Jun.	.07	Nov.	.02	Mar.	.01
Washington, D. C....	1,000	Potomac River ø	5	Jun.	.03	Nov.	.02	Mar.	.01
Pottstown, Pa........	30	Schuylkill River ø	10	Jun.	.05	Nov.	.04	Mar.	.02
Norristown, Pa.	55	Schuylkill River ø	5	Jun.	.07	Nov.	.04	Mar.	.04
Philadelphia, Pa.....	1,100	Schuylkill River ø	4	Jun.	.12	Nov.	.04	Mar.	< .01

*Numerals indicate the following: (1) chlorination; (2) partial chlorination; (3) partial aeration; (4) coagulation, sand filtration, and partial chlorination; (5) prechlorination, coagulation, sand filtration, partial chlorination, and activated-carbon treatment for taste and odor control; (6) coagulation, sand filtration, and chlorination; (7) coagulation and chlorination; (8) prechlorination, coagulation, sand filtration, and partial chlorination; (9) prechlorination, two-stage coagulation and sedimentation, sand filtration, and partial chlorination; and (10) coagulation, sand filtration, partial chlorination, and activated-carbon treatment for taste and odor control.

◆ No treatment methods.

‡ Little or no upstream pollution

ø Repeated stream use for both water supply and waste disposal.

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contents were found in summer and spring, respectively.

The occurrence of ABS in surface water of the United States is shown in Table 4.

Data regarding the ABS content in domestic raw sewage and sewage effluents are not readily available. McGauhey and Klein, (1959) indicate that ABS in domestic raw sewage might range from 5 to 10 ppm, whereas McKinney and Donovan (1959) suggest values of ABS ranging from 1 to 10 ppm. Specific measurements of ABS in raw sewage have been reported as listed in Table 5 (Association of American Soap and Glycerine Producers Analytical Subcommittee Report, 1961). With regard to water pollution, it is more significant to determine the ABS in sewage effluents actually discharged into streams or rivers. The authors have analyzed various sewage effluents from plants around Colorado and other parts of the United States (Table 6).

With regard to the ABS content of household septic tank effluents, only limited data are available. Recent results (Bendixen, 1961) of grab samples from septic tanks at Dallas, Texas and Phoenix, Arizona indicate ABS contents that range from 0.04 to 64 ppm. Data are listed in Table 7.

Table 4.—*ABS in surface water of the United States*

Location	ABS (in ppm)	Reference
Illinois River		
Summit to Pekin, Ill	0.5 to 1.3	Hurwitz and others (1960)
Franklin Bridge, Peoria, Ill	0.2 to 0.9	Harmeson (1961)
Kaskaskia River		
Bondville to Ficklin, Ill	0.04 to 0.12	Morgan and Engelbrecht (1957)
Cass River		
Frankenmuth, Mich	0.0 to 0.1	Olivier (1961)
Clinton River		
Utica, Mich	0.5 to 0.6	Olivier (1961)
Raisin River		
Blissfield, Mich	0.0 to 0.2	Olivier (1961)
Dundee, Mich	0.0 to 0.1	Olivier (1961)
Rouge River		
Rockford, Mich	0.0 to 0.2	Olivier (1961)
Ohio River		
Anderson Ferry, Ohio	0.01 to 0.59	Weaver and Coughlin (1960)
Willo Island, West Va	0.08 to 0.31	Orsanco (1962)
Newell, West Va	0.0 to 0.2	Orsanco (1962)
Ravenswood, West Va	0.0 to 0.2	Orsanco (1962)
Warsaw, Ky	0.0 to 0.3	Orsanco (1962)
Golconda, Ill	0.0 to 0.2	Orsanco (1962)
Grand Chain, Ill	0.0 to 0.1	Orsanco (1962)
Missouri River	0.01 to 0.04	Walton (1960)
Mississippi River	0.02 to 0.04	Walton (1960)
Schuykill River	0.04 to 0.08	Walton (1960)
Marais des Cygnes River		
Ottawa to Osawatomie, Kansas	0.08 to 1.3	Culp and Stoltenberg (1953)
Neosho River		
Emporia to Oswego, Kansas	0.14 to 0.24	Culp and Stoltenberg (1953)
Chanute to Erie, Kansas	0.5 to 1.7	Task Group Report (1954)

Table 5.—*ABS in domestic raw sewage*

Location	ABS in ppm
Oakland, California	4.4
San Francisco, California	7.0
Chatham-Madison, N. J.	3.3
West New York, N. J.	13.8
Cincinnati, Ohio	3.1
Mt. Washington, Ohio	3.3
Ponca City, Oklahoma	11.8

The most serious effect of ABS pollution concerns the impairment of the quality of ground water aquifers. ABS may infiltrate through soils into ground water from various sources as listed below:

(1) laundromats

(2) cesspool and septic tank drainage fields

(3) sewage settling ponds

(4) irrigation ditches, streams, and rivers containing sewage

(5) sewage oxidation ponds.

Table 6.—*ABS in sewage effluents of United States*

Location	ABS in ppm
Denver, Colorado plant......	3.0 to 7.5
Clear Creek (0.5 mi. above junction with S. Platte River).	3.0
Sand Creek (North of Denver).	6.0
N. Washington plant (2 mi. north of Denver).	4.2
Northwest Utilities Plant (Thornton, Colo.).	11.0
Brighton, Colo. plant........	6.0
South Adams, Colo. plant	13.0
Tucson, Arizona plant.......	4.2
Trenton, N. J. plant	3.0
Hamilton Township, N. J., plant.	8.5
Southwest plant, Chicago, Ill..	7.5

Table 7.—*Analysis of individual septic tank effluents (Dallas, Texas and Phoenix, Arizona) for* ABS, PO_4 *and* COD

Sample code	ABS in ppm	PO in ppm	COD in ppm
FHA-1.......	0.04	0.3	45
FHA-2.......	23	38	543
FHA-3.......	64	44	445
FHA-4.......	37	46	619
FHA-5.......	11	29	359
FHA-6.......	7	14	236
FHA-7.......	6	27	313
FHA-8.......	10	32	564
FHA-9.......	10	23	354
FHA-10......	23	38	630
FHA-11......	7	18	275
FHA-12......	25	38	798

The possibility of ABS pollution of ground water by infiltration is influenced by a number of factors such as:

(1) distance between source of pollution and aquifer

(2) soil characteristics

(3) population density and number of septic tanks per square acre

(4) velocity and direction of water flow in both the saturated and unsaturated zones.

The pollution of ground water aquifers is wide-spread in geographical distribution. In 1960, it was reported (Amer. Water Works Task Group Report 2450-R, 1960) that sewage or ABS pollution occurred in 26 out of 48 States in the United States. It is probably safe to state that detailed "detective" work would indicate that pollution of ground water by ABS is found in every State. In a ground water reconnaissance study (Kiser, 1959), ABS was found in well water at Norfolk, Virginia; Miami, Florida, Minneapolis, Minnesota; Huntsville, Alabama; La Crosse, Wisconsin; and Albuquerque, New Mexico, in concentrations that ranged from 0.4 to 4.1 ppm. In another study (Harmeson, 1961) ABS pollution of ground water from infiltration of river water was observed in Illinois; the maximum amount of pollution occurred in wells closest to the river. The most serious outbreak of ABS ground water pollution has been noted in areas of densely populated housing developments that contain individual wells and individual sewage disposal systems; these areas are represented by ground water pollution on Long Island and in the Minneapolis–St. Paul area. The ABS content of wells polluted from laundromat waste at Brookhaven, Long Island, ranged from about 0.37 to 28.9 (Lauman, et al, 1960). In another study (Davids and Flynn, 1960) it was indicated that 35 percent of 600 well waters analyzed were polluted with ABS and speculated that 17,000 wells in Suffolk County would eventually become polluted. As of September 1960, about 30,000 wells of the 63,000 analyzed showed pollution of ABS in the Minneapolis–St. Paul area (Woodward and others, 1960).

The above paragraphs are sufficient documentation with regard to the prevalence of ABS pollution in various realms of water supply or waste water. The U.S. Geological Survey in cooperation with the Federal Housing Administration has been investigating various aspects of ABS pollution with concentrated effort in soil-water environments. The major part of the investigation consisted of studies on the physicochemical properties of surfactant solutions, adsorption of ABS on soil minerals and soils, filtration of ABS from treated sewage by soils for saturated flow, and natural infiltration of ABS and other constituents in diluted sewage near Denver, Colorado. A limited amount of study was given to the biodegradation of ABS and to the analytical determination of ABS. The results of this investigation are given in this report.

ANALYTICAL METHODS FOR THE DETERMINATION OF SURFACTANTS

From the viewpoint of amount of surfactants produced and probably occurring in natural water anionics and nonionics are the most important in the order mentioned. Colorimetric methods and infrared spectroscopy have been emphasized for the determination of anionics in water such as the alkyl sulfates and the alkyl benzene sulfonates. Other methods (paper chromatography, gas chromatography, ion exchange, ultraviolet spectrometry, and neutron activation analysis) have been mentioned in the literature but to date have received only limited consideration. For the determination of anionic surfactants (including ABS) in water by either colorimetric or precipitation techniques, a vast number of indicators or reagents have been employed such as pontamine fast red 8 BNL (Wijga, 1949), protein-bromocresol purple (Loomeijer, 1954), bromophenol blue (Hoyt and Walker, 1953), basic fuchsin (Wallin, 1950), dichlorofluorescein (Iwasenko, 1953), methyl green (Moore and Kolbeson, 1956), o-tolidene (Scales and Kemp, 1939; and Harris, 1943), toluidine blue (Terayama, 1952), o-toluidine (McGuire and others, 1962), p-toluidine hydrochloride (Marron and Schifferlie, 1946; Stupel and Segesser, 1951, and House and Darragh, 1954), and methylene blue (Jones, 1945; Epton, 1947; Evans, 1950; Degens and others, 1953; Weatherburn, 1954; Longwell and Maniece, 1955; Fairing and Short, 1956; Slack, 1945; Webster and Halliday, 1959; Bolton and others 1961; and Hill and others, 1962).

The use of the methylene blue procedure has remained the most popular since its inception (Jones, 1945) because of its simplicity. However, the method does not give an unequivocal determination of ABS. When ABS and other anionic surfactants are in solution, their reaction with methylene blue forms a blue-colored salt. The salt is soluble in chloroform and the amount of surfactant can be determined quantitatively on the basis of intensity of the color with the use of a spectrophotometer. The method is reported (American public Health Association and others, 1960) to detect ABS concentrations in the range 0.025 to 100 mg/1 (milligrams per liter). Both organic and inorganic constituents interfere with this method, which is not totally specific for the sulfonated benzene ring. Organic sulfates, sulfonates, carboxylates, phosphates, and phenols form complexes with methylene blue, and inorganic cyanates, chlorides, nitrates, and thiocyanates form ion pairs with this compound to give positive interferences. Other organics, such as amines, may offer negative interferences through competition with methylene blue for a reaction. Details of the methylene blue method have been presented (American Public Health Association and others, 1960).

There are a number of variables to be considered in employing the methylene blue method for ABS determinations such as (1) pH of extraction—if the extraction is done above pH 7, various hues of pink, blue-pink, or violet are obtained. This colorimetric effect can be removed by acidifying the solution (Jones 1945 and Longwell and Maniece, 1955). The cause of the pinkish color can probably be attributed to impurities in the methylene blue dye and will be considered below. The recommended procedure (American Public Health Association and others, 1960) suggest that the extraction be accomplished by making the solution alkaline and then acidifying before the shaking procedure. (2) Time of measurement of complex after extraction—the authors have studied the stability of the ABS-methylene blue complex by measuring spectrophotometrically the change in absorbency (A) at concentrations of 10 ppm and 1 ppm as ABS as a function of time (t). The results are shown in figure 1 (Wayman, 1962-a). At 10 ppm and 1.0 ppm,—dA/dt is 7×10^{-4} and 2×10^{-4} absorbency units per minute, respectively. The data indicate that the extracted complex decays continuously with time; the stability is greater at lower ABS concentrations. The degradation of the extracted complex might be explained by photochemical or oxidation influences. Little error seems to be introduced if the absorbency is measured within 60 minutes after extraction. This observation should be considered in day to day analyses of ABS. Many laboratories frequently extract 6 to 8 samples in an 8-hour day and measure the absorbency at the end of this period; obviously poor precision would be attained with such a technique. (3) purity of methylene blue dye—the importance of the type of dye used with the method has already been indicated (Wayman, 1962-a). A dye that displays maximum absorbency at the wavelength of interest should be used. Figure 2 shows the change of absorbency for a variety of dyes in solutions containing 0.5 ppm and 1.0 ppm of ABS. Of these dyes, Eastman

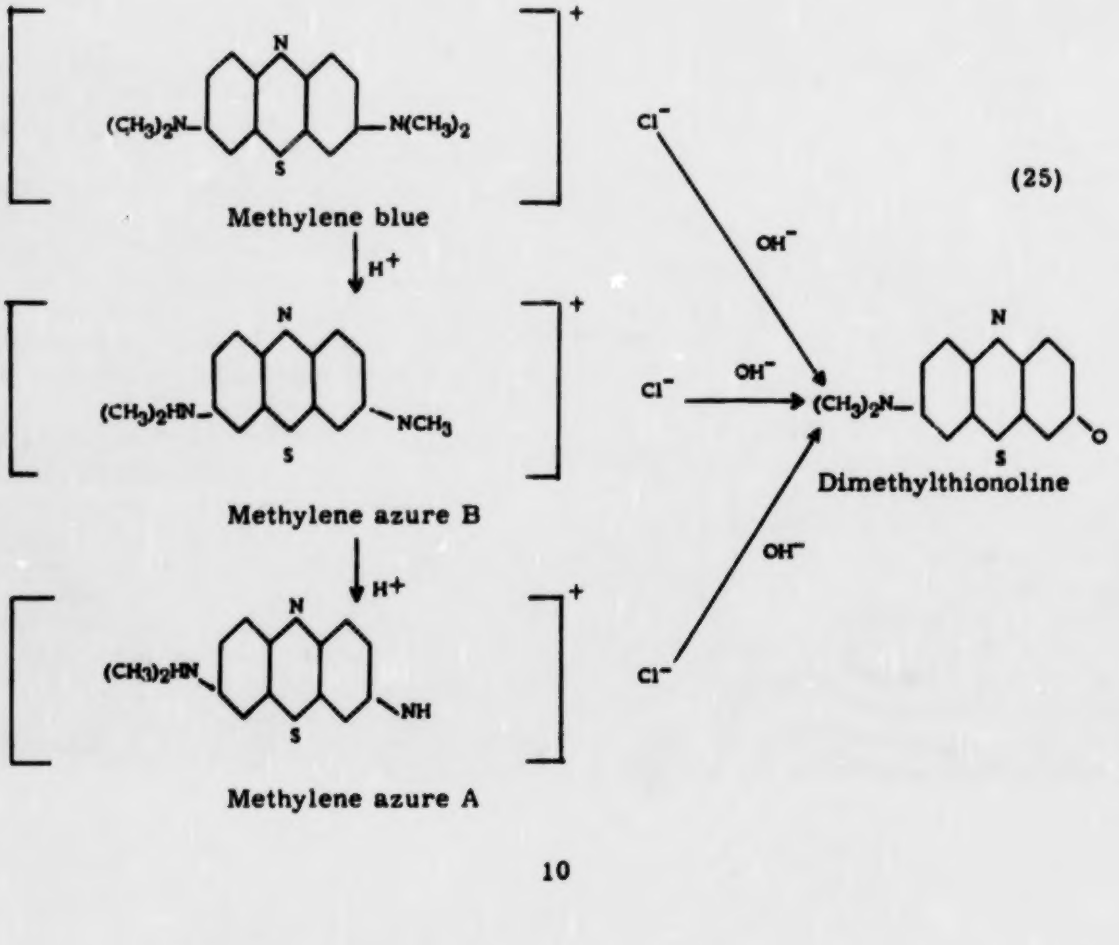
P-573 of Fisher Na-652 give maximum absorbancy and should be preferred with this method. Many problems are inherent in the application of organic dyes as indicators for analytical determinations. Organic dyes may deteriorate with time, and the impurities contained from batch to batch may vary; these factors should be considered in selection of a dye for analytical purposes. A profuse literature is available on impurities in methylene blue and reasons for its instability most, of which, have been summarized by Abbott (1962):

(a) below pH 9.5 aqueous solutions of methylene blue at room temperature are definitely stable but decompose by de-methylation in basic solution, the rate and amount being a function of hydroxyl ion concentration.

(b) methylene blue is so readily oxidized that it cannot be produced without impurities of methylene azure B, methylene azure A, and dimethylthionoline. These impurities are essentially products of deterioration of methylene blue and account for its staining properties; methylene blue in an extremely purified form displays poor staining properties. Colorimetric entities of methylene blue might also be related to this phenomenon of impurity. The formal oxidation scheme of methylene blue can be represented as

(c) methylene blue azures form hydroxides that are slightly soluble in water giving blue solutions; the hydroxides readily form anhydrides which impart red solutions in chloroform. A chloroform solution of these hydroxides can be mixed with carbonated water with production discoloration (solvent phase) and formation of blue color in the water phase. Alkaline treatment of methylene blue produces a red chloroform-soluble complex that becomes blue upon filtration through cotton. If alkaline solutions of the chloroform extract of methylene blue or methylene azure B are exposed to the atmosphere, the color changes from red to violet to blue. Thus, the chloroform extract of commercial methylene blue give the four complexes (methylene blue, methylene azura A, methylene azure B, and dimethylthionoline); the amount of each complex depends on the degree of impurity in the dye. Abbott (1962) has suggested that the methylene blue method can be improved in sensitivity by about 15 percent by the following: methylene azures are removed from two portions of water, alkaline buffer and methylene blue solutions by chloroform and the red extracts are rejected. One portion is acidified to act as a wash solution, and the sample is added to the other portion, further extractions being carried out in a manner similar to that used in the Webster and Halliday method (1959).

(4) pre-extraction versus direct extraction—



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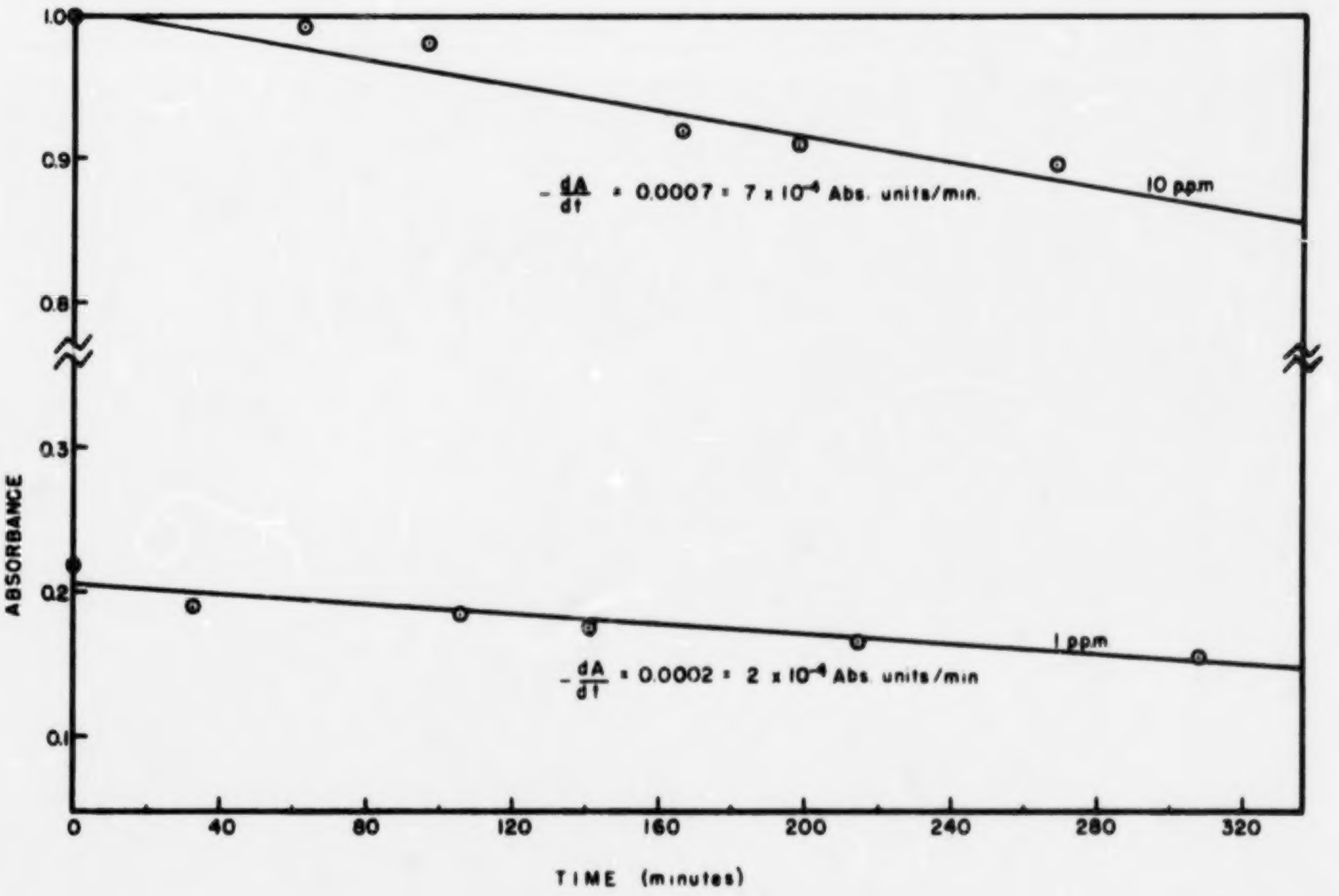


Figure 1.—Influence of time of measurement on ABS absorbancy determination.

in its standard form, the methylene blue procedure, per se, extracts the total amount of anionic-active substances in solution through direct extraction. By a pre-extraction step, positive interferences in the methylene blue procedure can be reduced. In this recommended procedure (Webster and Haliday, 1959), the 1-methylheptylamine salt of ABS is extracted with chloroform and light petroleum as a purification step in the procedure. When applied to sewage effluents and river water, the pre-extraction procedure gave results about 35 percent lower than those obtained by direct extraction; these results are also in good agreement of the unequivocal determination of ABS by the infrared procedure. (5) effect of temperature on stability of complex—because temperature was believed to exert some influence on stability of the colorimetric complex, a series of extractions on ABS solutions (standard method) containing 1 ppm were made at room temperature and stored at 10°C, 20°C, and 35°C (Wayman, 1962a. Measurement of the absorbance of these solutions indicated that temperature in this range had no significant influence on complex stability. (6) effect of pre-oxidation by chrome-sulfuric acid—in a recent paper (Hill and others, 1962) have utilized chrome-sulfuric acid as an oxidant to remove surfactants other than ABS and other ions from solution before use of the methylene blue method. When this oxidation step is used, the methylene blue method seems less subject to interferences from inorganic ions and certain surfactants. The accuracy of the methylene blue method for ABS determinations can be influenced by a number of variables, most of which, were enumerated above. The precision of the method seems to depend on the concentration of ABS, reflecting some type of a bias in the procedure. Table 8 shows that the standard error of estimate increases with concentration (Wayman, 1962a). On the basis of 60 samples, standard errors of estimate were determined as 0.75 ± 0.13 and 2.50 ± 0.3 ppm of ABS. The number of samples upon which other precision data are based is not readily available.

Because the methylene blue method is not entirely specific for ABS determination, an

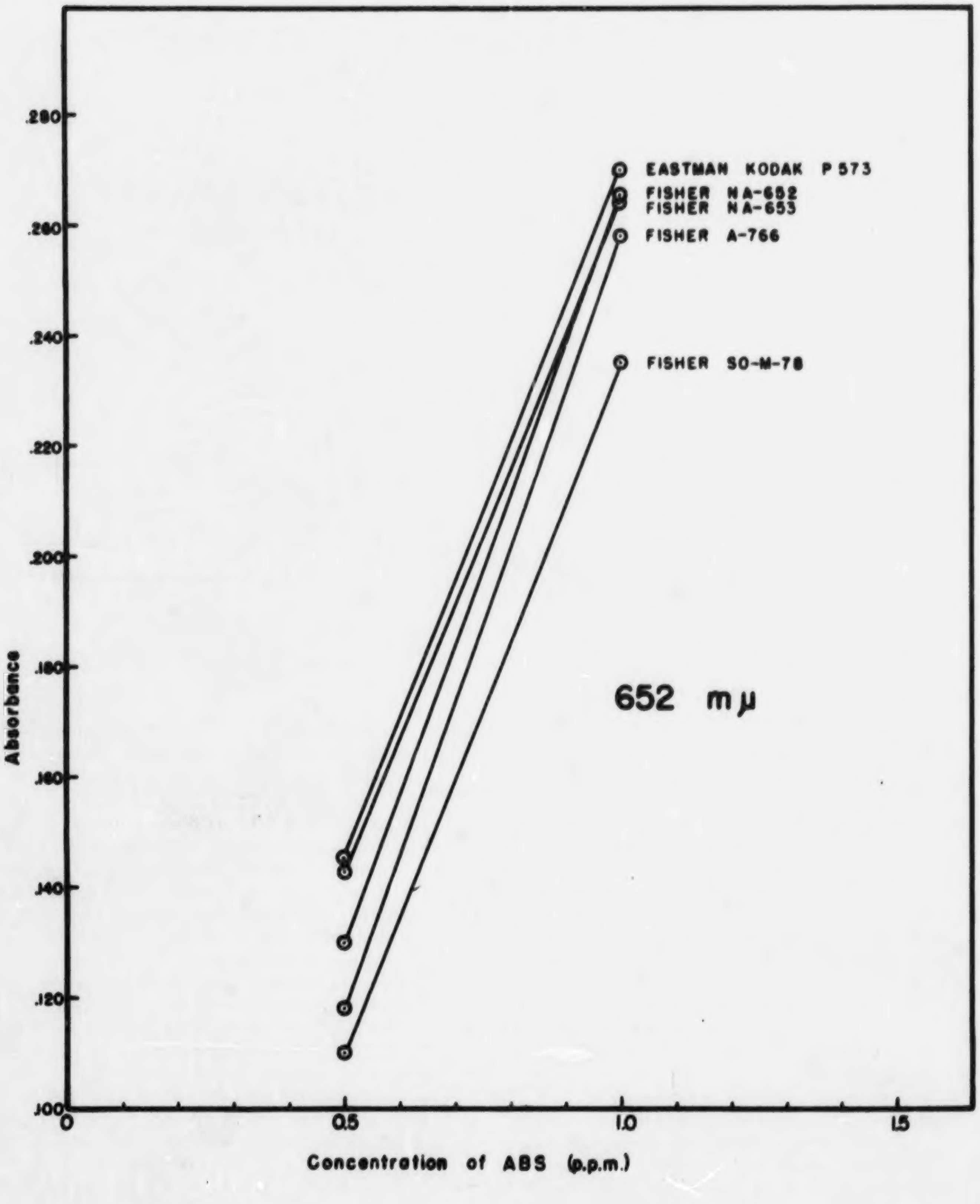


Figure 2. —Effect of dye type on absorbancy determination.

Table 8.—*Standard error of estimate of ABS at various concentrations.*

ABS concentration (ppm)	Standard error of estimate				Report
	Field samples		Laboratory samples		
	Source	Ppm	Type of water	Ppm	
0.40			Distilled	0.05	American Public Health Service and others (1960).
.75			do	.13	B. B. Ewing (written communication, 1960).
2.22			Tap	.18	American Public Health Service and others (1960).
2.50			Deionized	.30	Wayman (1962-a).
.35		0.04			Cohen (1961).
1.00		.12			Do.
1.25		.19			Do.
1.31	River water.	.25			American Public Health Service and others (1960).

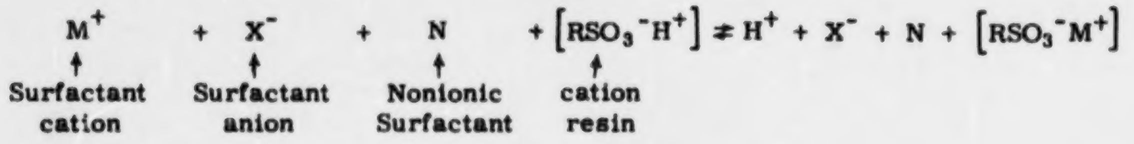
infrared referee method was developed (Sallee and others, 1956) to give an unequivocal identification of ABS. The method depends upon the adsorption of ABS on activated carbon and its removal (desorption) with alkaline benzene-alcohol. Then, acid hydrolysis decomposes phosphates, organic sulphates, and other hydrolysates; a petroleum ether wash of the alkaline solution extracts hydro-carbons, alcohols, sterols, and other constituents. ABS is then extracted quantitatively by chloroform as the 1-methylheptylamine salt to eliminate it from inorganic salts and water-soluble organics. The ABS-amine salt is then placed in carbon disulphide or carbon tetrachloride solvent and the absorbance is meas- by an infrared spectrophotometer at the wavelength region 9.6 to 9.9 microns (μ). The infrared procedure has been extended (Ogden, Webster, and Halliday, 1961) for the identification of biologically hard and soft surfactants. Total alkylbenzenesulfonate is determined in carbon disulfide at 9.9μ and biologically hard ABS in carbon tetrachloride at 7.31μ. The amount of biologically soft ABS is obtained by difference of the absorbances.

In addition to colorimetric and infrared procedures for determination of anionics (including ABS), some investigators have considered the use of ultraviolet spectrometry for the analysis of ABS. The application of an ultraviolet source to various type of ionic surfactants gave data on the classification of 100 commercial compounds consistent with that reported in the literature (Reid and others, 1955). A detailed method for the quantitative determination of ABS at concentrations in excess of 10 ppm has been described (Kelley and others, 1959). Substitution of the sulfonate and alkyl groups on the phenyl chromophore gives a strong absorption region between 210 to 230 millimicrons (mμ) with a maximum at 224 mμ for 11 ppm of ABS and a weaker band between 250 to 270 mμ for 108 ppm of ABS. Positive interferences are caused by benzene toluene, and xylene sulfonates. Nonionics such as alkyl phenoxypolyoxyethylene ethanol types and their anionic sulfate ester derivatives cause interference by strong absorption in this region. Interference from detergent "builders" such as phosphates, silicates, carbonates, and carboxymethylcellulose is considered insignificant; in addition alkyl sulfates give no interference. Though the method seems to give acceptable results without measurable interference, its application to natural waters would require a preconcentration step to improve sensitivity. The method is reported to be independent of pH. Ultraviolet spectrometry has also been applied to studies involving adsorption of ABS on charcoal (Morris and Weber, 1962). By dilution of solutions containing about 35 ppm of ABS, an absorption maximum was obtained at 225 mμ. At 220 mμ p-toluenesulfonate displays an absorption maximum. Benzenesulfonate causes no interference in this region. It is indicated that this method cannot be applied to analysis of ABS in waste water because of marked interference from other solutes. In another application of ultraviolet spectrometry for the determination of ABS (Ling and Greenberg, 1963), it is indicated that ABS is strongly absorbed between 220 and 230 millimicrons and can be estimated to 0.5 mg/1 in the absence of interferences. When interferences are present (especially nitrate ions), these can be eliminated by a series of evaporations after appropriate treatment with acids and bases followed by extraction with ethanol.

ABS has also been analyzed in mixtures with nonionics by either two-stage ion exchange or mixed-bed ion exchange. The two-stage method for analyzing anionics (ABS) and nonionics has been described in detail (Ginn and Church, 1959) and involves passage of the mixture through a strong acid cation exchange resin (Dowex 50 X 4, a sulfonated styrene-divinylbenzene copolymer) to remove cations and to convert the anionics to the acid form. The effluent from this step contains acidified anionic and nonionic material which is then passed through a weakly-basic anion resin (Duolite A-7), containing functional groups of primary, secondary, and tertiary amines. The anions are removed by the formation of acid salts with the amine functional groups. Nonionic surfactants are unaffected and pass through with the effluent. The anionic surfactant is eluted with alcholic caustic solution and finally isolated as the sodium salt by a salting-out technique. The reactions involved in the procedure are:

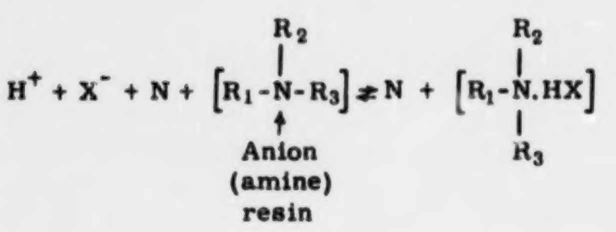
Another method combining ion exchange and titration has recently been published (Takahama and Nishida, 1957) for determining ABS in the presence of nonionics, inorganic salts, chelating agents, organic builders, and bleaching agents. Dried samples are extracted with isopropanol with filtration of insolubles. The filtrate is then passed through a cation exchange resin (Amberlite IR-120) and anionics are titrated by alkali microvolumetrically. Because chlorides are extracted by isopropanol, corrections must be made by silver nitrate titration. Inorganic salts, organic builders, chelating agents and bleaching agents cause no interference. Ion exchange has recently been combined with ultraviolet spectrometry to separate mixtures of short- and long-chain sulfonates (Chem. and Eng. News, March 18 1963 p. 42). Solutions containing mixtures of about 1.0 milligram quantities of toluenesulfonate (TS), xylenesulfonate (XS), and dodecylbenzenesulfonate (DBS) are passed through a cation exchange resin (Dowex 50-X2); TS and XS can be removed from the resin with respect to DBS by elution with 1.0 molar aqueous ammonium sulfate solution. Then DBS is recovered from the resin by elution with only water. The eluents can be identified by ultraviolet spectrometry at 222 mμ.

CATION REMOVAL



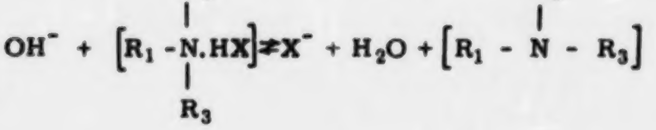
$$\underset{\substack{\uparrow\\\text{Surfactant}\\\text{cation}}}{M^+} + \underset{\substack{\uparrow\\\text{Surfactant}\\\text{anion}}}{X^-} + \underset{\substack{\uparrow\\\text{Nonionic}\\\text{Surfactant}}}{N} + \underset{\substack{\uparrow\\\text{cation}\\\text{resin}}}{[RSO_3^-H^+]} \rightleftharpoons H^+ + X^- + N + [RSO_3^-M^+] \qquad (26)$$

ANION (ABS) REMOVAL



$$H^+ + X^- + N + \underset{\substack{\uparrow\\\text{Anion}\\\text{(amine)}\\\text{resin}}}{[R_1\text{-}\overset{\overset{R_2}{|}}{N}\text{-}R_3]} \rightleftharpoons N + [R_1\text{-}\underset{\underset{R_3}{|}}{\overset{\overset{R_2}{|}}{N}}.HX] \qquad (27)$$

ELUTION OF ANION



$$OH^- + [R_1\text{-}\underset{\underset{R_3}{|}}{\overset{\overset{R_2}{|}}{N}}.HX] \rightleftharpoons X^- + H_2O + [R_1 - \overset{\overset{R_2}{|}}{N} - R_3] \qquad (28)$$

Either of the ion exchange methods or a combination of these may offer a partial solution or improvement to colorimetric procedures, especially when nonionics carrying some residual negative or positive charge are suspect.

Neutron activation analysis has recently been applied to the determination of ABS in water (Wayman 1963-a). Neutron activation analysis is a method for detecting traces of chemical elements from the alpha, beta, or gamma activity emitted after bombardment by thermal or slow neutrons. Sulfur in ABS is the source of a beta-emitter; therefore, the beta activity from other sources in solution must also be evaluated. In water, major sources of beta activity are sulfur, chlorine, phosphorus, and sodium from reaction such as:

$$S^{34}\ (n,\gamma)\ S^{35} \qquad (29)$$

$$Cl^{35}\ (n,p)\ S^{35} \qquad (30)$$

$$P^{31}\ (n,\gamma)\ P^{32} \qquad (31)$$

$$S^{32}\ (n,p)\ P^{32} \qquad (32)$$

$$Cl^{35}\ (n,\alpha)\ P^{32} \qquad (33)$$

The beta activity from Na^{24} can be eliminated because of its relatively short half-life (14.97 hours), or by chemical separations. Equation (29) in the above series can be used to describe a typical neutron capture reaction:

$$S^{34} + n^1 \rightarrow S^{35} + \gamma \qquad (34)$$

indicating the capture of a neutron and the ejection of a gamma photon in the Formation of S^{35} by neutron activation. The other reactions can be depicted in a similar manner. Sulfur in ABS was determined by this method from solutions containing 0.86, 0.09, and 0.009 ppm of surfur in alkyl benzene sulfonate (99 percent pure). Sulfur was determined by irradiating 10-ml aliquots each of the detergent solutions and sulfuric acid (sulfur standard) for 1000 kwh at a thermal neutron flux of 1.0×10^{13} neutrons $cm^{-2} sec^{-1}$ in a TRIGA reaction. After irradiation, sulfur and phosphorus carriers were added to the samples, and the sample solutions were boiled to fumes non-radioactive species isotopic with the radioactive transmutation product. Then $BaSO_4$ and $MgNH_4PO_4 \cdot 6H_2O$ were finally precipitated for counting S^{35} and p^{32}, respectively, on a low background beta counter (0.3 counts per minute). Chlorine was determined by irradiation of 5-ml aliquots for 500 kwh at a thermal neutron flux of 1.8×10^{12} neutrons cm^{-2} sec^{-1} in a TRIGA reactor. Chlorine was detected instrumentally using the 1.65 Mev gamma-ray of 37-minute Cl^{38}. The slow neutron capture reaction involved in this case is:

$$Cl^{37}\ (n,\gamma) Cl^{38} \qquad (35)$$

Results from the irratiations are summarized in Table 9. Discrepancies exist between the amount of sulfur added and the amount found. Determination of sulfur by S^{35} was both inconsistent and inaccurate (due to radioactive contaminants in the $BaSO_4$ precipitates), whereas when sulfur was determined by P^{32} there was a discrepancy but it was a consistent one. High results for sulfur may have been caused by significant but variable removal of sulfonate from the ion exchange resin during deionization of the water. more likely, a small phosphorus impurity in the detergent might have caused the discrepant values found by P^{32}. If the detergent contained about 0.5 percent P, the results would be in exact agreement. Because of its very low concentration, chlorine would not have caused any significant interference (0.1 ppm Cl would only be equivalent to 0.007 ppm S, determined as P^{32}). The specific activities of the phosphorus and sulfur fractions were 75 cpm (counts per minute) per μg (microgram) P and 1.0 cpm per μg S, respectively. The P^{32} activity varied linearly with the amount of sulfur added, but the amounts of sulfur indicated by the P^{32} values were about three times the amounts of sulfur originally added. As little as 0.01 ppm of ABS sulfur in water can be detected, provided chlorine and phosphorus have been removed to eliminate interferences from the $P^{31}\ (n,\gamma)\ P^{32}$ and $Cl^{35}\ (n,\gamma)\ P^{32}$ reactions. The most sensitive reaction for determining sulfur is $S^{32} (n,p)\ P^{32}$. When both S and P are in water, the use of a double irradiation technique at

Table 9.—*Sulfur and chlorine determination from neutron activation analysis.*[+]

	ppm S			ppm Cl
Sample	Added	Found via S^{35}	Found via P^{32}	
A	0.86	≥ 4.6	2.7	≤ 0.2
B	.09	≥ 5.6	.27	.1
C	.009	≥ 2.4	.029	.1

[+] These analyses were carried out in cooperation with the Activation Analysis Service of the General Atomic Division, of General Dynamics Corporation, San Diego, California.

various fast to slow neutron flux ratios might be used (Bouten and Haste, 1962). The method also is non-specific for ABS because it determines total sulfur. Hence, ABS must be concentrated by a foaming device or separated in water from other forms of sulfur (sulfate, sulfite, and sulfide) by anionic chromatography, the latter being recently suggested (Iguchi, 1958). The method shows promise for the determination of ABS, but additional work is required to evaluate the precision, detection limit, and influences of various ions in solution on sensitivity in addition to determining ABS in natural water. The method might have the highest degree of success in ground water because of a limited amount of interference.

Paper chromatographic procedures have been developed for identification of synthetic detergents in mixtures (Blandin and Desalme, 1954). This technique has been applied successfully to separate normal saturated alkyl sulphates when the adjacent members differ in chain length by two carbons atoms (Holness and Stone, 1955). Mixtures of n-octyl, n-decyl and n-dodecyl sulphates were separated by ascending paper procedures using 15 percent aqueous ethanol, whereas 40 percent ethanol was used to separate n-tetradecyl, n-hexadecyl and n-octadecyl sulphates on Whatman No. 1 paper at 30°C. The anionic spots were developed by spraying with an aqueous solution of pinacryptol yellow. Under ultraviolet light, these spots appear as bright orange on a pale yellow background. The detection limit seems to be about on μg (microgram). The method can be modified for separation and identification of sulfonates. A similar technique to the one above has been employed to separate normal sodium alkyl sulphates containing twelve to eighteen carbon atoms (Franks, 1955). Whatman No. 1 filter paper is saturated with a long-chain fatty alcohol (cetyl alcohol) as stationary phase applied as one percent ethanol; the mobile phase was an aqueous solution of ethanol saturated with cetyl alcohol, the concentration of ethanol employed depending upon the concentration of sulphate to be separated. After drying, the chromatogram is immersed in 0.5 percent cuprice acetate and sprayed witha 0.05 percent solution of rhodamine 6 GB. The alkyl sulphate spots appear as crimson on a pink background in normal light and as dark purple on a yellow background in ultraviolet light. R_f values decrease with increase in the number of carbon atoms in the chain and range from 0 to 1.0 for ethanol concentrations of 50 to 75 percent. The method can be applied also to sulfonates. Considering the bulk of effort that has been given to colorimetric procedures, it would seem that the possible determination of ABS by paper chromatography or electrophoresis has been overlooked and should be stressed and evaluated in the future. No elaborate equipment or instrumentation is required and the method is rapid.

Gas-liquid chromatography has recently been employed to determine ABS (Knight and House, 1959). The method involves desulphonation of the hydrophilic portion of the surfactant ion (SO_3) from the hydrophobic portion alkylbenzene. A few grams of sodium dodecylbenzenesulfonate (average molecular weight 348) are reacted with phosphoric acid at 215°C for 90 minutes. After a series of extractions and filtrations, about 70 to 80 percent of the theoretical amount of the alkylbenzene can be recovered. The rate of desulfonation increases with decrease in molecular weight of the alkyl group. Various isomers of the alkylbenzenes can be separated by gas-liquid chromatography and identified on the basis of their retention times on columns. The method can be utilized for both branched-chain and straight-chain types of ABS. Other investigators have also applied gas chromatography to the analysis of alkylbenzenes (Olson, 1960; Spencer and Johnson, 1960; Swisher and others, 1961). The macrodesulfonation method of Knight and House (1959) has recently been modified for microdesulfonation and adapted to gas chromatography (Swisher, 1962a and Setzkorn and Carel, 1960). The desulfonation procedure seems to have no effect on reaction of the original alkylbenzene sulfonate; however; some of the intermediate degration products (carboxyl, keto, aldehyde, and hydroxyl groups) might be destroyed (decarboxylation, dehydration, cyclization, olefin formation, and cracking during desulfonation which should be detectable by gas chromatography (Swisher, 1962b). The microdesulfonation method is particularly applicable to biodegradation studies using river water or diluted sewage effluents. The present type of surfactants (tetrapropylene ABS) used in commercial detergents gives 75 to 100 major components and perhaps several hundred minor components detectable by gas chromatography (Swisher, 1963). Although gas chromatography gives a prolific amount of qualitative information regarding surfactant structure, its application to quantitative determinations of ABS in water would probably become too cumbersome. However, the combination of gas chromatography with infrared or ultraviolet spectrometry might be the ultimate answer to the specific determination of ABS in water.

NONIONICS

Because nonionic surfactants presently command about 20 to 25 percent of the synthetic detergent market, some consideration will be given to the determination of these substances in water.

The amount of oxyethylene in polyoxyethylene glycols can be determined by decomposition of the polyglycol with hydrogen iodide through the volumetric reactions of ethyl iodide and ethylene with standard solutions of silver nitrate and bromine, respectively (Morgan, 1946). Polyethylene glycols have also been determined gravimetrically by the combined use of barium chloride, hydrochloric and phosphomolybdic acids (Oliver and Preston, 1949); similarly these glycol ethers have been precipitated by a synthetic tannin prepared as a condensate of resorcinol and glucose in the presence of sulfuric acid (Haakh and others, 1951). Polyglycols have also been precipitated with phosphotungstic acid (Etienne, 1957).

Titration procedures have also been employed to determine nonionics. Ethylene glycol can be analyzed after oxidation by periodic acid by titration with sodium thiosulfate and potassium iodide using starch as an indicator (Toilet Goods Assoc., 1952). Ethylene oxide can be precipitated in a known excess of potassium ferrocyanide before back titration with zinc sulfate (Schonfeldt, 1953). Ethylene glycols have also been determined qualitatively in aqueous solution (Davis and others, 1955; and Karabinos, 1955) or in organic solvents (Tanaka, 1957 by titration employing a 2.0 percent aqueous phenolic solution.

The use of certain physical properties has been used to determine ethylene glycols. The mole ratio of ethylene oxide to alkylphenol has been investigated in terms of refractive indices (Mayhew and Hyatt, 1952). A method based on mixed melting points and weight of sample was studied to evaluate the number of ethylene oxide units in detergents (Karabinos and others, 1955).

Nonionics have also been determined by colorimetric and spectrophotometric procedures. Gravimetry has been combined with a colorimetric method in the analysis of ethylene glycols by complexion with silicotungstic and phosophomolybdic acids (Shaffer and Critchfield, 1947). The amylose fraction of potato starch can be used to complex polyoxyethylene stearate. The amylose portion of the complex is then employed in the formation of the colorimetric complex with iodine. The method is reproducible to ± 0.010 percent for solutions as dilute as 0.05 percent (Mac Allister and Lisk, 1951). Ultraviolet spectrometry at 310 mμ (methyl cellosolve blank) has been applied to the analysis of nonionic surfactants in sewage (Heatley and Page, 1952). The precipitate formed when nonionic surfactants react with phosphomolybdic acid can be measured with the aid of a spectrophotometer for concentrations as low as 0.1 ppm. Inorganic salts cause no interference but alkyl sulfates, alkylarylsulfonates, and carboxymethylcellulose give high, positive results (Stevenson, 1954). Polyoxyethylene type surfactants can also be determined by chemical treatment with an acidic solution of carbonyl-free, methanolic, 2,4-dinitrophenylhydrazine; addition of 10 percent alcoholic potassium hydroxide forms a purple complex that can be measured at 560 mμ (Gatewood and Graham, 1961).

Paper chromatography has been applied to nonionics. One of the earlier studies (Kume and others, 1953) of this method was used to determine the average molecular weight of polyethylene oxides in the range 1000 to 5000. In another investigation (Gallo, 1954), polyhydeoxyethylene compounds were identified on the basis of a yellow precipitate formed with $(BiSCN)K_3$. The R_f values are high with poor separation of compounds.

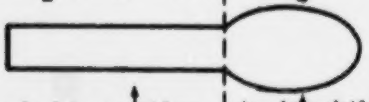
Recently, high resolution nuclear magnetic resonance has been used to identify various ethylene oxide condensates (Flanagan and others, 1962). The method is rapid (½ hour) and requires only small amounts of sample (0.1 ml) but gives only average values.

Various aspects of ion exchange or related methods have been investigated for separation of anionics and nonionics as indicated in the section under anionics (Ginn and Church, 1959; and Takahama and Nishida, 1957). Salting out chromatography has been studied on nonionic surfactants with sodium chloride and other alkali metal salts in solution (Doscher and others, 1951). Adsorption columns have also been used (Green and others, 1954); emulsions containing nonionics were quantitatively separated by adsorption on a column of mixed Zeokarb 225 and De-Acidite FF. The surfactants are removed by elution with 50 percent aqueous ethanol followed by trichloroethane. Similar studies were made using animal charcoal but the desorption of surfactant cannot be effected.

CHARACTERISTICS OF SOLUTIONS CONTAINING SURFACTANTS AND DETERGENTS

An unsophisticated definition of a *detergent* is a substance that will cleanse, remove, or wash-away similar or disimilar particles adhering to each other. The composition and types of detergents were presented in another section. With regard to water pollution, the surfactant (surface-active agent) is the portion of a detergent demanding considerable attention. A *surfactant* is a chemical coumpound that has a strong affinity to be attracted at a surface or interfacial area; this surface or interfacial area for consideration in this report may be represented as liquid-air or solid-liquid. The liquid-air interface finds practical significance in foams observed on surface water and the solid-liquid interface pertains to the possible adsorption of a surfactant (ABS) on natural minerals. A surfactant ion consists of two parts: (1) hydrophilic-that which as an affinity or desire to remain in water and (2) hydrophobic-that portion which has a phobia to get out or no desire to remain in water. The specific portions of a surfactant ion such as dodecyl-bensenesulfonate (C_{12}ABS) can be represented as follows:

$$\left[C_{12}H_{25}\text{-}C_6H_4 \,\vdots\, \text{-}SO_3\right]^{-1} \tag{36}$$



where $C_{12}H_{25}$ is an alkyl chain containing twelve carbon atoms
C_6H_4 is the benzene ring
SO_3 is the sulfonate

and the entire ion displays anionic behavior in water with a negative charge of one. Surfactants in water contribute largely to the modification of solution properties. In solution, surfactants influence surface tension, critical micelle concentration, dispersion and flocculation, and foaming. Each of these properties will be considered separately.

SURFACE TENSION

Surface tension is that physico-chemical property which enables a surface to assume a surface area minimum; this minimum in surface area is accomplished by molecular cohesive forces. Surface molecular forces tend to be attracted inward at a greater rate than its escaping tendency at the surface; therefore, this difference produces a contracted surface with minimum surface area or minimum surface free energy. The Helmholtz free energy of a liquid system can be expressed by

$$dF = - Sdt - PdV + \gamma_0 dA + \Sigma \mu dn \tag{37}$$

F = free energy
T = absolute temperature
P = pressure
V = volume
γ_0 = surface tension of the pure liquid
A = surface area
μ = chemical potential
n = number of molecules

Consider a system at constant temperature, volume, and number of molecules; then

$$\gamma_0 = \left(\frac{\partial F}{\partial A}\right)_{T,V,n} \tag{38}$$

From (38) it can be seen that a contracting surface involves the quantities γ_0 be positive, ∂A be negative producing ∂F as negative. A negative value for ∂F means a minimum in free energy (surface contraction). It can also be shown (Davies and Rideal, 1961) that the Helmholtz free energy per unit area of surface (F^s) is equal to   from the relation

$$\gamma_0 = F^s + A\left(\frac{\partial F^s}{\partial A}\right)_{T,V,n} \tag{39}$$

For a one-component liquid, F^s does not depend on the area and the second term in (39) becomes zero and

$$\gamma_0 = F^s \tag{40}$$

It can similarly be shown that

$$\gamma_0 = G^s$$

the Gibbs excess free energy at constant T and P. It is generally considered that practical considerations show G^s and F^s to be identical. G^s and F^s have dimensions of dynes cm^{-1} and ergs cm^{-2} which are identical.

The total surface energy of a liquid is equivalent to the total potential energy of the molecules necessary to form 1 square centimeter of liquid surface in excess of that which the same molecules would possess in the interior of the liquid (Davies and Rideal, 1961). The total surface energy excess (U^s) over the Helmholtz free energy excess can be determined from the expression

$$U^s = \gamma_0 - T\left(\frac{\partial\gamma_0}{\partial T}\right)_{n,V} \qquad (41)$$

For pure water at 25°C

$$\gamma_0 = 72 \text{ ergs cm}^{-2}$$

$$\frac{\partial\gamma_0}{\partial T} = -0.154$$

$$U^s = 72 - 298(-.154) = 117.8 \text{ ergs cm}^{-2}$$

Therefore, the total surface energy excess exceeds the surface tension at 25°C by the amount 45.8 ergs cm^{-2}.

When surfactants such as depicted in (36) are in water, the hydrophilic portion orients its head in water and the hydrophobic portion orients its tail out of water as shown in figure 3. Thus, ABS ions tend to adsorb at the air-water interface as a monomolecular film as shown in figure 3. The actual type of adsorption determines whether the surface tension will increase or decrease that of the solvent or water system. Many organic solutes, especially surfactants are positively adsorbed at the surface and lower the surface tension; positive adsorption simply means the solute is more concentrated in the surface film than in the bulk of solution. Conversely, many inorganic solutes are negatively adsorbed and increase the surface tension; in this case the solute is more concentrated in the bulk of solution than in the surface. The Gibb's adsorption equation is a thermodynamic artifice usually employed to calculate the surface concentration excess or deficiency as compared to the concentration in the bulk solution: (constant temperature and pressure)

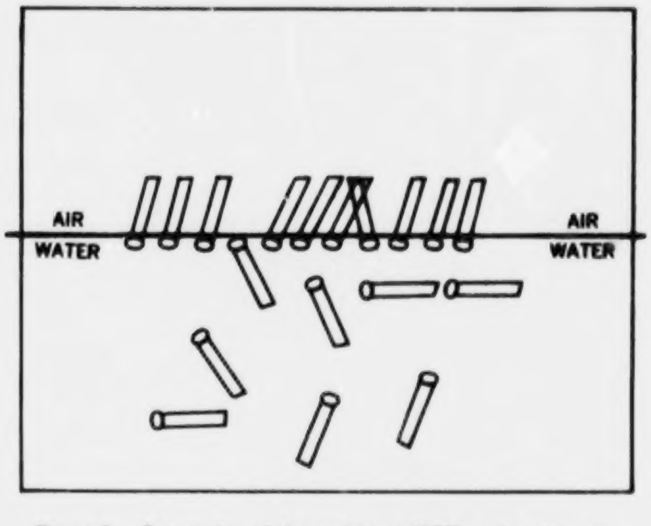


Figure 3. —Orientation of the surfactant (ABS) at the air-water interface.

$$d\gamma = \sum_{n+1}^{k} \Gamma_i \, d\mu_i \qquad (42)$$

$d\gamma$ = change in surface tension

Γ_i = surface excess or deficiency over the solution concentration of the i th component

$n+1$ = the condition for n=1 is the dividing surface ($n = 1$, $\Gamma_1 = 0$)

k = total number of components

If the chemical potential is expressed in terms of the activity, then

$d\mu_i$ = RT d ln a_i

R = gas constant

a_i = the thermodynamic activity

for which the surface excess becomes (43)

$$\Gamma_i = -{}^1/RT\left(\frac{\partial\gamma}{\partial \ln a_i}\right)_{T,P,\text{all a's except}}$$

$a_i = 1$ and i

Then for dilute solutions a_i can be approximated by concentration (c_i) and converting natural logs to log to the base 10

$$\Gamma_i = -\frac{1}{2.303\,RT}\,\frac{\partial\gamma}{\partial \log c_i} \qquad (44)$$

Thus from a knowledge of the surface tension-concentration gradient for a specified temperature, Γ_i will be positive if $\frac{\partial\gamma}{\partial \log c}$ is negative which appears for a decrease in surface tension with concentration and vice versa.

The Gibbs adsorption equation employed to show the behavior of surfactants at the air-solution interface with respect to thermodynamic activity or concentration was originally derived for ideal, dilute solutions (Gibbs, 1928, p. 219). Later workers who have used surface tension measurements as a means of studying the behavior of surfactants at air-solution interfaces have disagreed as to the validity of the equation. For nonionic surfactants, the Gibbs adsorption seems to be satisfactory (Hutchinson, 1948). For ionizable compounds, some investigators found that the surface excess (the amount of surfactant at the air-solution interface compared to the bulk solution) calculated from surface tension measurements amounts to only half the value measured directly (Brady, 1959a; Salley and others, 1950). Pethica (1954) showed that the equation is valid only in an excess of a neutral salt. Davies (1952) achieved satisfactory results in calculating the surface excess of cetyltrimethylammonium ions at the oil-water interface, and Matuura and others (1958) found that the surface excess of alkyl sulfates could be calculated reasonably well for concentrations below the critical micelle concentration (that concentration at which single ions begin to form into a cluster of ions).

One of the writers has applied the Gibbs adsorption equation to solutions containing the surfactant Na alkylbenzenesulfonate (Na ABS) between 2°C and 35°C (Wayman, 1963b). For a dilute solution of sodium alkylbenzenesulfonate ($Na^{+}\ X^{+1}$), the Gibbs adsorption equation can be expressed as

$$d \ = RT\Gamma_{Na^{+1}}\, d\ln C_{Na^{+1}} - RT\Gamma_{x^{-1}}\, d\ln C_{x^{-1}} - RT\Gamma_{H^{+1}}\, d\ln C_{H^{+1}} \tag{45}$$

where

$d\gamma$ = change in surface tension

R = gas constant

T = absolute temperature

$\Gamma_{Na^{+1}}$ = adsorption of sodium ion at the surface

$\Gamma_{x^{-1}}$ = adsorption of the ABS ion at the surface

$\Gamma_{H^{+1}}$ = adsorption of the hydrogen ion at the surface

$C_{Na^{+1}}$, $C_{x^{-1}}$, $C_{H^{+1}}$ = various ionic concentrations

If the pH is kept constant and sodium ion is not adsorbed at the surface, then $\Gamma_{Na^{+1}} = \Gamma_{x^{-1}} = \Gamma_{HX}$ $C_{Na^{+1}} = C_{x^{-1}} = C_{NaX}$, and equation (45) reduces to

$$\Gamma_{HX} = \frac{1}{2.303RT} \cdot \frac{d\gamma}{d \log C_{NaX}} \tag{46}$$

Thus, the surface excess, Γ_{HX} (adsorption at the surface), can be calculated from equation (46) if the surface tension is measured at various ionic concentrations.

Figure 4 shows the change in surface tension at various concentrations of Na ABS (99 percent pure) for five different temperatures ranging from 2°C to 35°C. For the temperature range studied, small changes in concentration produce large changes in surface tension for ABS concentrations of as much as the critical micelle concentration (about 1000 ppm). At this concentration, ABS has less tendency to accumulate because the air-solution interface has become saturated. Surface excesses were calculated from slopes of the surface tension—log ABS concentration (figure 4) and the data are plotted in figure 5. The data indicate that the Gibbs adsorption equation is not strictly obeyed throughout the entire range of concentration and temperature but no serious deviations occur up to the critical micelle concentration. In fact, the surface excess varies less than a factor of two (2.5 to 3.8×10^{-10} moles per cm^2) for the conditions studied. It is also obvious that surface excess cannot become more concentrated than the critical micelle concentration. ABS displays excellent surfactant properties on the basis of these calculations.

The determination of surface excess has certain practical applications:

(1) it can be used to indicate the degree of surfactant and

(2) it can be used to calculate the cross sectional area of a surfactant ion or molecule necessary in evaluation of monolayer or multilayer adsorption on solid mineral surfaces.

The data from figure 5 were used to calculate the area occupied per detergent molecule at the air-solution interface from the expression:

$$S = \frac{1}{\Gamma N} \tag{47}$$

where S = area occupied per molecule

N = Avogadro's number = 6.02×10^{23} molecules per mole

Γ = surface excess in moles per cm^2

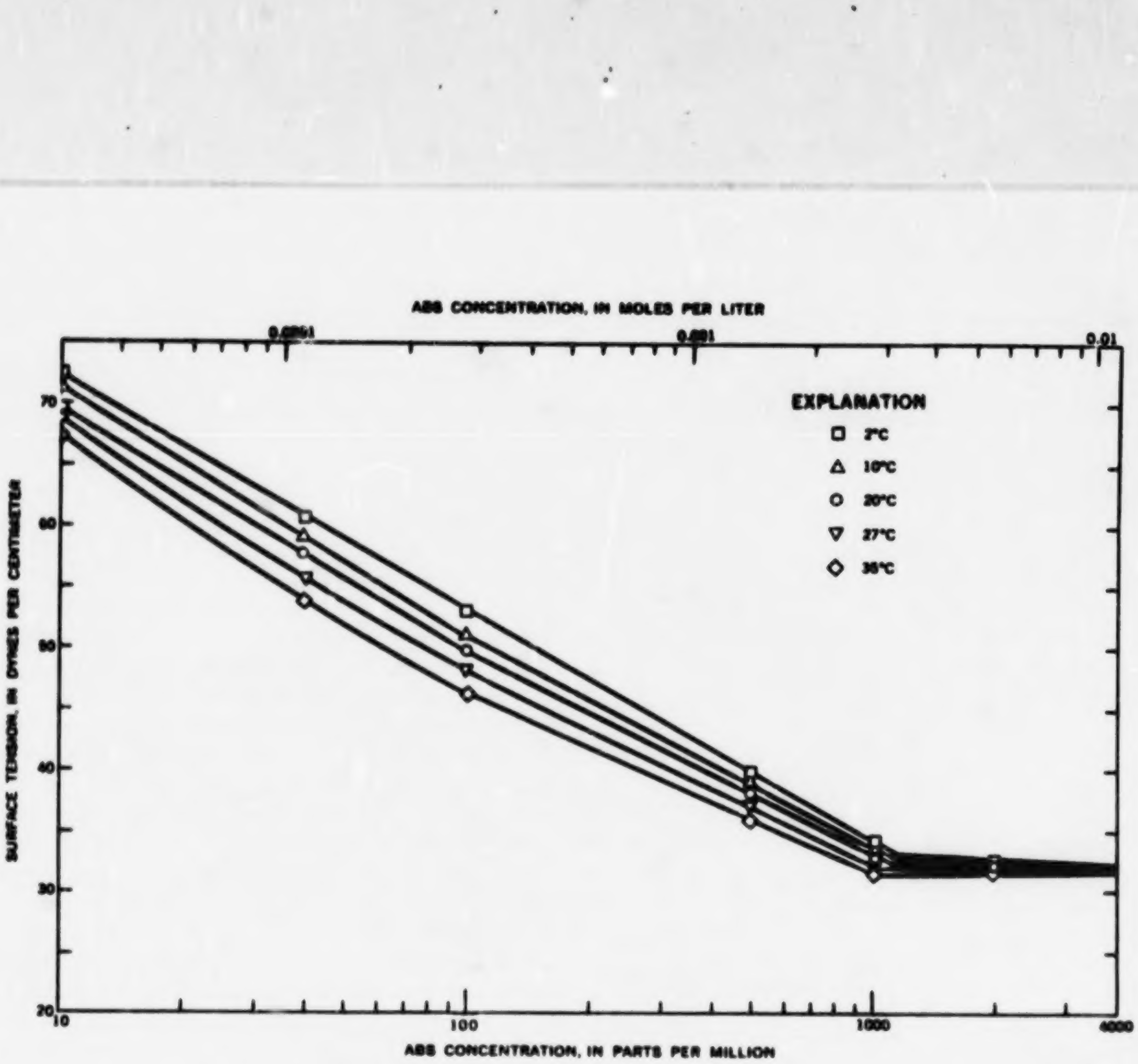


Figure 4.—Relation of surface tension to concentration of ABS and to temperature.

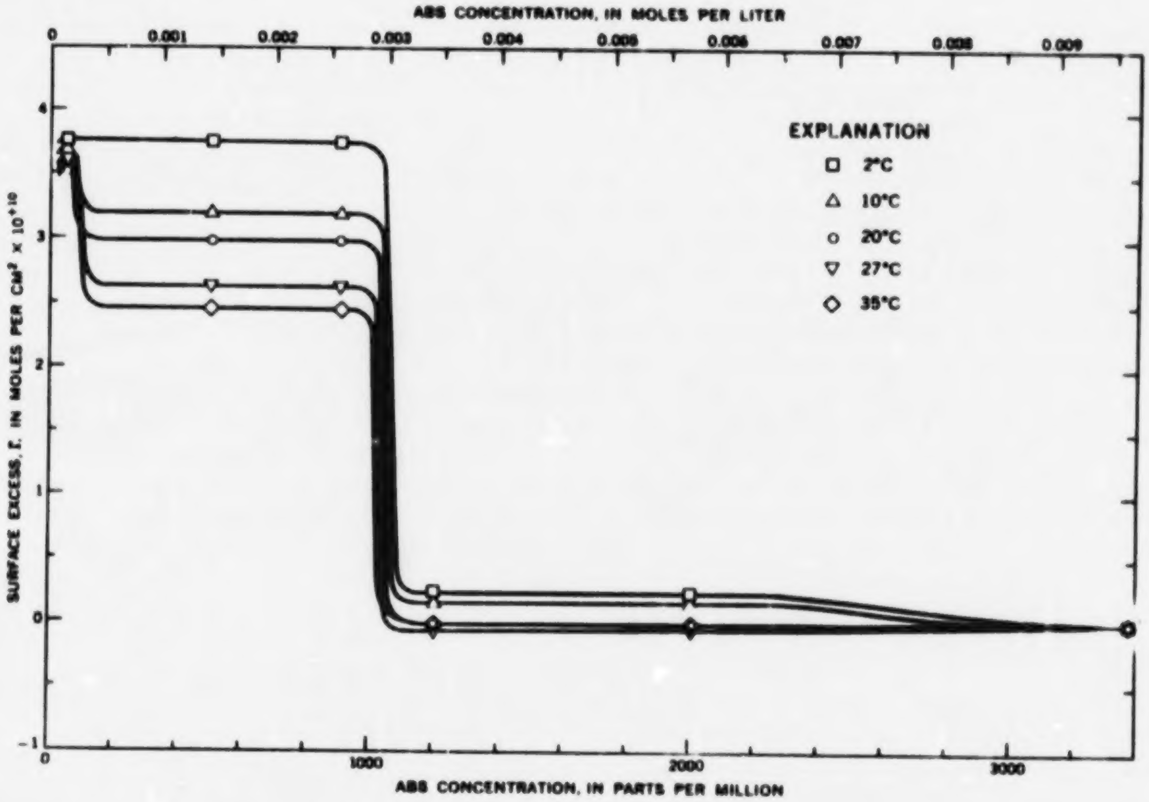


Figure 5.—Relation of surface excess to concentration of ABS and to temperature.

The calculation was made for a solution containing 50 ppm of Na ABS at 20°C. Thus,

$$S = \frac{1}{3.5\times10^{-10} \text{ moles per cm}^2 \times 10^{-16} \text{cm}^2 \text{ per A}^2 \times 6.02\times10^{23} \text{ molecule per mole}} = 47.4\text{A}^2 \text{ per molecule}$$

where A^2 (1 square angstrom unit) is equivalent to 10^{-16} cm^2. For similar surfactant solutions, the location of the hydrophilic group on the hydrocarbon chain has a pronounced influence on S (Meader and Criddle, 1953). These investigators found the following values for S in dilute solutions of ABS: sodium 1—dodecylbenzenesulfonate ($S = 38A^2$ per molecule), sodium 2-dodecylbenzenesulfonate (49.5), sodium 6-dodecylbenzenesulfonate (120), and hygroscopic dodecylbenzenesulfonate (56). Thus, the surface area per molecule seems to increase for a twelve carbon atom alkyl chain from benzene ring attachment at carbon atom number one toward carbon atom number six (center of the chain) for such types of ABS molecules. On the basis of this data, the value of 47.4 A^2 per molecule obtained in our study probably consisted on the average of an ABS molecule of sodium 2-dodecylbenzenesulfonate.

The application of surface area of the ABS molecule to adsorption studies on quartz sand has been recently reported (Wayman, 1962b). Theoretically, ABS is adsorbed as a monomolecular layer on the surface of sand grains. To calculate the area required for a monolayer of coverage by ABS, a molecular weight of 350 was assumed. The amount of surface required per ion was based on that calculated from equation (47) which amounted to 47.4 A^2 per molecule. If the number of ABS ions in 100 ml of an aqueous solution containing 10 mg ABS is considered then

$$\frac{1\times10^{-2}\text{g} \times 6.02 \times 10^{23} \text{ ions per mole}}{350 \text{ g per mole}} = 1.72 \times 10^{19} \text{ ions}$$

are available. The surface area of the solid, X, which would be covered by a monolayer of this number of ions, is the product of the number of ions and their cross-sectional area or

$$\frac{X = 47.4 \text{ A}^2 \times 1.72 \times 10^{19} \text{ ions}}{\text{ion}} = 82{,}044 \text{ cm}^2$$

Thus, a total available surface area of the solid mineral is 82,044 cm^2, if completely covered with a monomolecular layer, can adsorb 10 mg ABS. To determine whether theory could be correlated with experiment, the adsorption of ABS on sized fractions of the "Ottawa Sand" was investigated as a function of time. About 95 percent of this sand ranges in size from 20 to 30 mesh. After grinding and separation by screening, 25-gram samples of the original material, +140, -140 + 270, -270 + 325, and -325 mesh fractions, and a blank (no solid present) were agitated at room temperature (26° ± 1°C) with 100 ml of an aqueous solution containing 10 mg ABS. These solutions were sampled periodically and their ABS content determined. The surface area for each size fraction was calculated, assuming spherical particles and a median grain size between sieves; the results are shown in Table 10 where a value of 30 microns was assumed for the -325 mesh fraction. Bikerman (1958, p. 223) has indicated that calculated surface areas and those measured by gaseous adsorption for silica sand of -270 mesh are accurate to the extent that does not differ by more than a factor of 2. The experimental results shows that an apparent equilibrium was established in about 120 hours for the -325 mesh fraction (figure 6). For the amount of surface area available on 25 grams of this fraction (25,000 cm^2) about 20 percent of the ABS could be removed from solution. The amount determined experimentally was about 35 percent. Figure 7 shows surface area plotted against adsorption capacity for calculated monolayer adsorption (B) and for the experimental determination (A). Because equilibrium adsorption on fractions of +325 mesh was slow and because the analytical method was limited in both detection limit and reproducibility, no apparent adsorption on these fractions was observed; therefore, these fractions are shown as extrapolated values (open circles) on figure 7 and appear as observed values in Table 10. Curve C in figure 7 represents calculated monolayer adsorption employing a value of $20A^2$ for the cross-sectional area of ABS. Meader and Criddle (1953) have shown that the cross-sectional area of ABS decreases with increase in length of the alkyl chain in terms of the

Table 10.—*Calculated surface areas and adsorption capacity of size fractions*

Mesh	Surface area (cm^2 per g)	Adsorption capacity (µg ABS per g solid)	
		Observed	Calculated
20-30	28	4	3.5
+140	60	8	8
-140+270	400	56	48.8
-270+325	700	100	85.5
-325	1,000	144	122

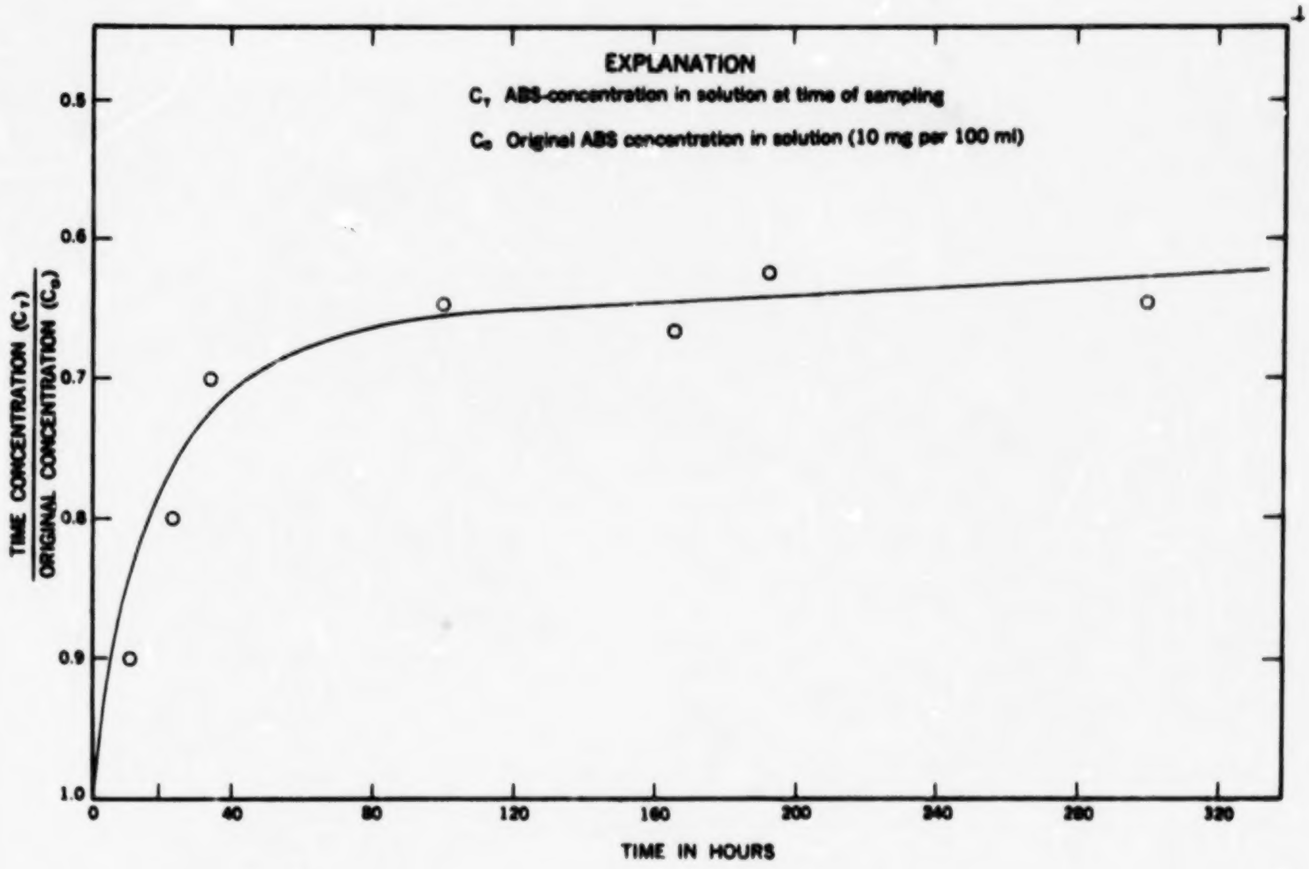


Figure 6.—Rate of approach to equilibrium adsorption of ABS on -325 mesh Ottawa Sand.

surface pressure. Surface pressure is the difference in surface tension between the solvent (water) and the surface tension when a surfactant (ABS) is in water or

$$\text{Surface pressure } (\Pi) = \gamma_o - \gamma \qquad (48)$$

γ_o = surface tension of water
γ = surface tension with ABS in solution

At low concentrations of ABS (10 to 50 ppm), surface pressures of about 10 dynes cm^{-1} produce cross-sectional areas of ABS ranging from about $50A^2$ $molecule^{-1}$ (dodecyl ABS) to $20A^2$ $molecule^{-1}$ (hexadecyl ABS). This range of values is covered in figure 7 and represents the practical limits encountered in surfactant ABS of commercial detergents. Figure 7 reveals some very interesting and practical relationships; for dodecyl ABS (curve B) adsorption takes place on sand grains at approximately a monolayer of coverage. For longer chain length ABS (hexadecyl ABS), adsorption on sand grains obtains at about 50 percent of a monolayer of coverage. For dodecyl type of ABS, essentially monolayer of coverage on "Ottawa Sand" has also been predicted and observed (Ewing and Banerji, 1962) similar to that in this study. Therefore, adsorption of commercial ABS on sand grains ranging from coarse to extremely fine takes place as a single (monolayer) of coverage. The completeness of this coverage decreases with increase in chain-length of ABS between dodecyl ABS and hexadecyl ABS. Ewing and others (1960) reported that "20–30 Ottawa Sand" adsorbed about 3.8 μg ABS per g (micrograms ABS per gram) for solutions containing 10 mg ABS per 1 (liter). Robeck (1961) reported that similar sands having surface areas of 49 cm^2 per g and 110 cm^2 per g adsorbed 3.0 μg per g and 10–20 μg per g, respectively, from solutions containing 10 mg ABS per 1. The data of these investigators are also plotted on figure 7 and appear in the range of adsorption for a monolayer of coverage. For sand particles having a surface area of 1,000 cm^2 per g, the observed adsorption capacity was 144 μg per g. This value is in reasonable agreement for the adsorption capacity of amorphous silica or silica gel (Ganguly, 1951). Grinding of the "Ottawa Sand" probably produced an amorphous layer, which has been observed by

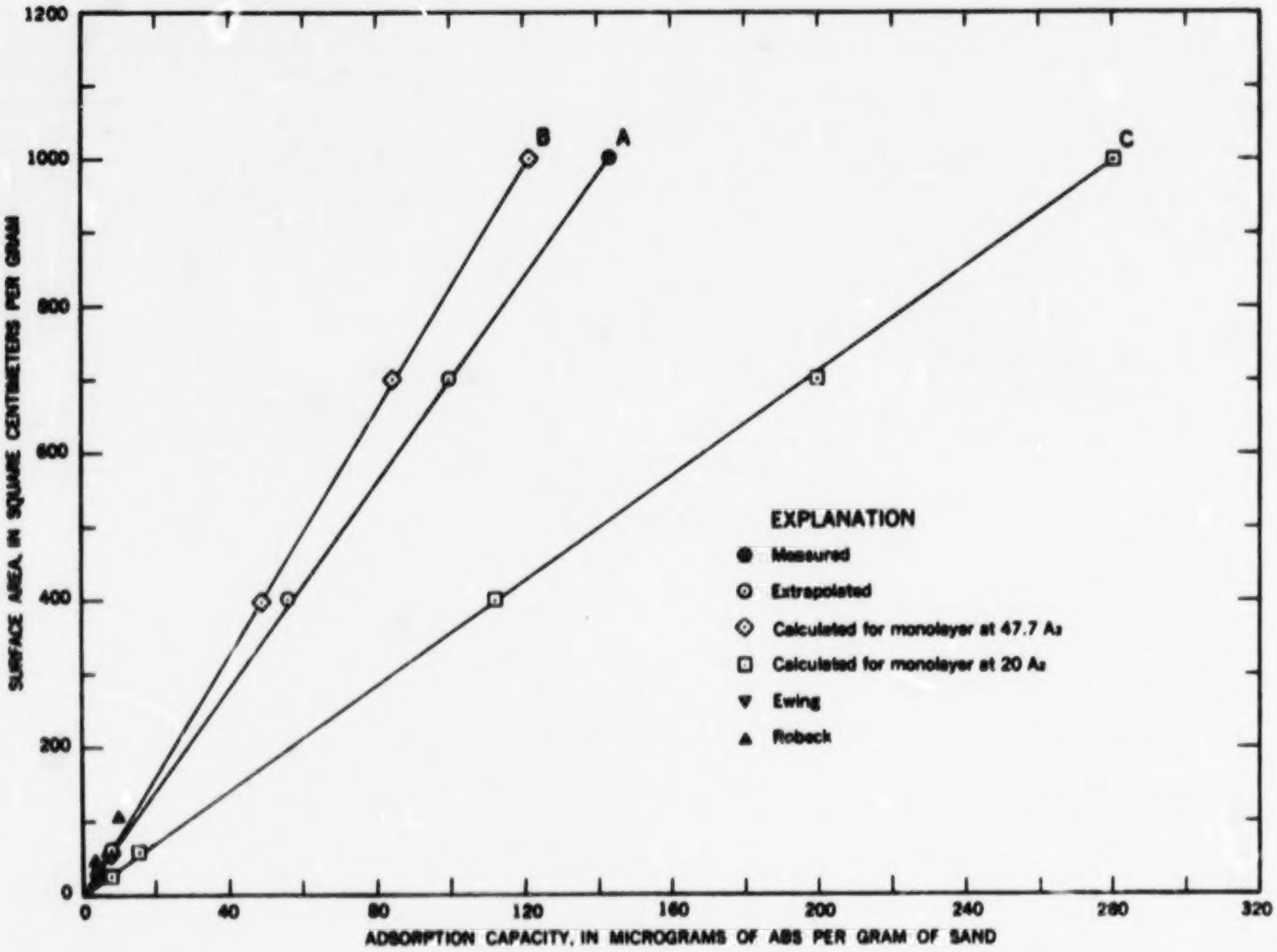


Figure 7.—Adsorption of ABS on "Ottawa Sand" as a function of surface area. A, experimental results; B, adsorption capacity calculated for a monolayer for cross-sectional area 47.4A^2; C, calculated for a monolayer for cross-sectional area of 20A^2.

many investigators such as Gordon and Harris (1955).

Surfactants in commercial detergents are responsible for lowering of the surface tension at the air-solution or solid-solution interface. Because this effect is essential to a complete understanding of water pollution problems, the surface tension of solutions containing anionic, cationic, and nonionic surfactants was measured (Wayman and others, 1962c). A Cassel type surface tensiometer was used employing the maximum bubble pressure technique (Weissberger, 1959, p. 797). In this technique, the surface tension (γ) can be calculated from the pressure required to rupture a liquid film placed upon a fine capillary opening or

$$\gamma = C_N \cdot P_B + S_C \qquad (49)$$

where C_N = capillary constant = 2.590
P_B = bursting pressure (g/cm^2)
S_C = surface tension correction factor which depends on P_B

The bursting pressure was calculated from the relation

$$P_B = H_M \cdot C_F (1 - A_F T_M - 20°C) \qquad (50)$$

where

H_M = height of liquid in manometer
C_F = density of manometer fluid = 1.000 g/cm^3 at 20°C
A_F = temperature coefficient of manometer fluid (°C^{-1})
T_M = manometer temperature (°C)

Table 11.—*Surface tension values used to evaluate* S_C

Temperature °C	Surface tension of solutions			
	Distilled water	Alkasene	Methylene iodide	Cetane
4°C	74.5	41.2	56.3	....
10°C	74.2	40.2	51.3	....
20°C	72.6	38.3	50.8	27.3
27°C	72.0	37.5	50.5	26.7
35°C	70.4	36.2	49.4	26.1

S_C must be evaluated by determination of γ for solutions of known surface tension values in terms of P_B. Table 11 shows the surface tension values used to evaluate S_C. Figure 8 shows the variation of the correction factor (S_C) with the most serious deviations between the true and the calculated values of surface tension occurring in the range 27 to 51 dynes cm^{-1} (P_B of 10 to 16 cm of manometer fluid.)

The influence of time of measurement on surface tension has been considered of importance (Niven, 1950, p. 55) especially in dilute surfactant solutions. The hydrogen ion concentration may contribute to rate of attainment of surface tension equilibrium (Burcik and Vaughn, 1951) because of hydrolysis effects; sulfonates are apparently stable and not readily susceptible to this effect (Niven, 1950, p. 28). Salts in solution with surfactants show a tendency to accelerate surface tension equilibrium. This effect was studied for the surfactant sodium laurate with 0.01N to 0.03N sodium chloride in solution (Burcik, 1950); it was concluded that this effect is prevalent for charged ionic surfactants in solution and not for nonionics. This effect can be analyzed in terms of the electrical double layer at the air-solution interface; as charged surfactants migrate to the surface, an ionic charge is developed which later tends to repel similar ionic species—accounting for reduced rates of attainment of equilibrium. If salts are in solution, the negative potential barrier is decreased because ions of opposite charge form part of a diffuse electrical double layer, thus permitting a more rapid diffusion of oppositely charged surfactants at the surface with increased rate of attainment of surface tension equilibrium. This effect has been observed for surfactant solutions containing sodium cetyl sulfate and sodium lauryl sulfate (Nutting and others, 1940). In this study the variation of the surface tension with time was measured for surfactant solutions containing 10 and 100 ppm of ABS and for 100 ppm of nonionic surfactant Tergitol. Figure 9 shows that the attainment of equilibrium values of surface tension for anionics with respect to time depends on concentration, whereas, those for nonionics seem to be quite stable. Standard procedure in this study was developed to record surface tension after ten minutes elapsed; under these conditions, surface tension measurements gave reproducible data. Figure 10 shows the variation of surface tension of solutions containing various anionic, cationic, and nonionic surfactants at 20°C. The data from Osipow (1962, p. 148) is included to show the reasonable agreement between this surfactant and Santomerse 85, surfactants each containing 85 percent ABS. The most significant point deduced from figure 10 is the rapid decrease in surface tension at low concentrations of ABS (below 50 ppm); this portion of the curve is most interesting because these concentrations most likely pertain to those most likely encountered in natural water. The data indicate that nonionic compounds are more surface active than either anionic or cationic compounds, which are about equally surface active. Santomerse E displays poorer surfactancy properties than other types of ABS because of its relatively short alkyl chain, which reduces surface activity. Figure 11 shows the variation of surface tension of a solid commercial detergent ("Tide") and a liquid commercial detergent for different concentrations at 20°C. The surface tension of commercial detergents is less than the pure surfactant (figure 10); however, the actual ABS concentration in commercial detergents is not readily known and part of this effect can probably be attributed to differences in surfactant concentration between the anionic ABS in figure 10 as compared to figure 11. Figure 12 shows the range of surface tension values for different commercial detergents at a concentration of 200 ppm. The values range from about 45 to 63 dynes cm^{-1}. The type of compound is specified for those where information was available. The wide range in surface tension

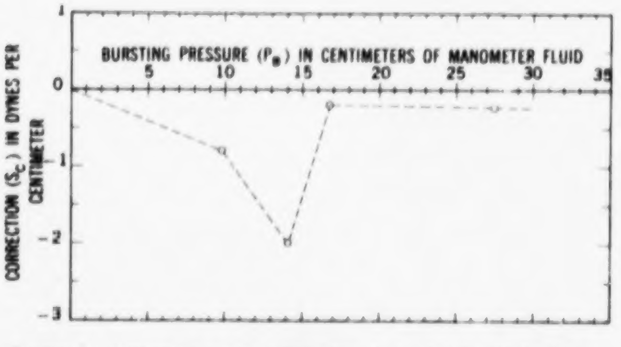


Figure 8. -Variation of the correction factor (S_C) with bursting pressure (P_B).

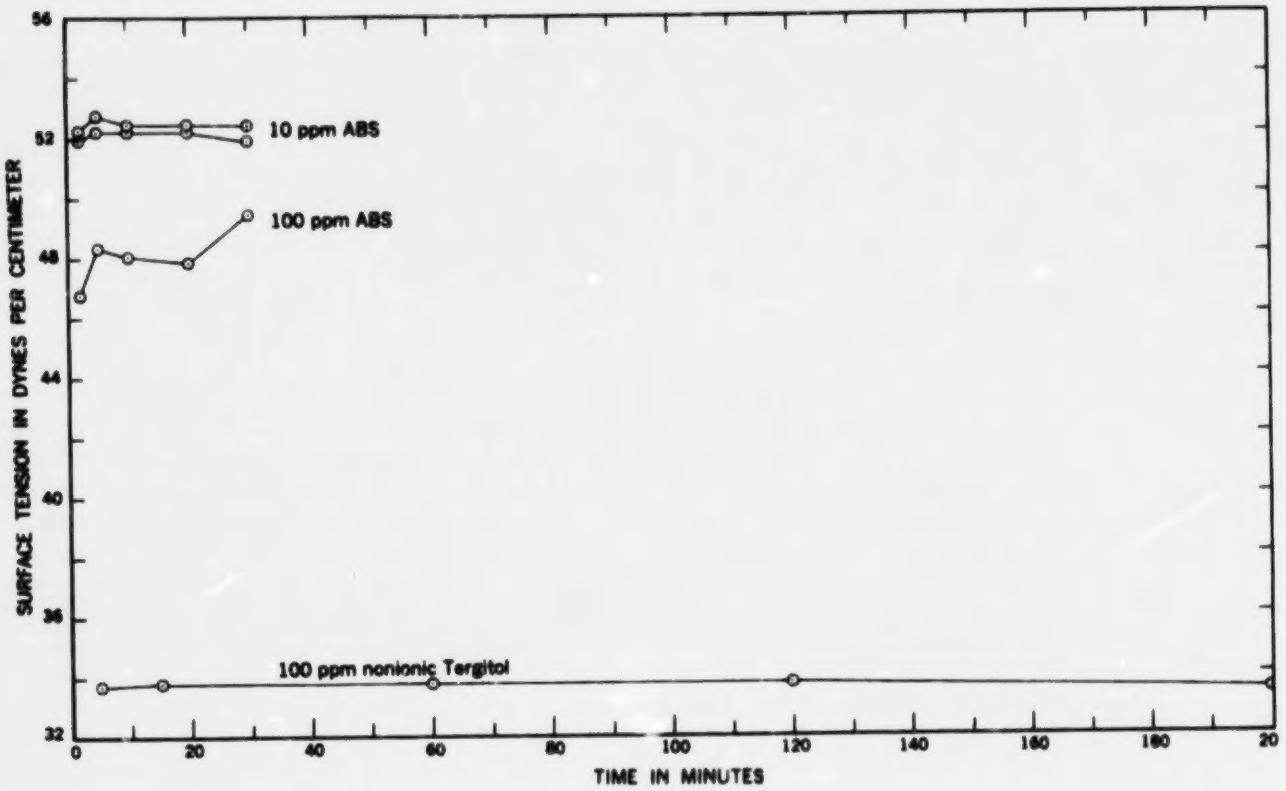


Figure 9. —Variation of surface tension with time as measured by a Cassel tensiometer.

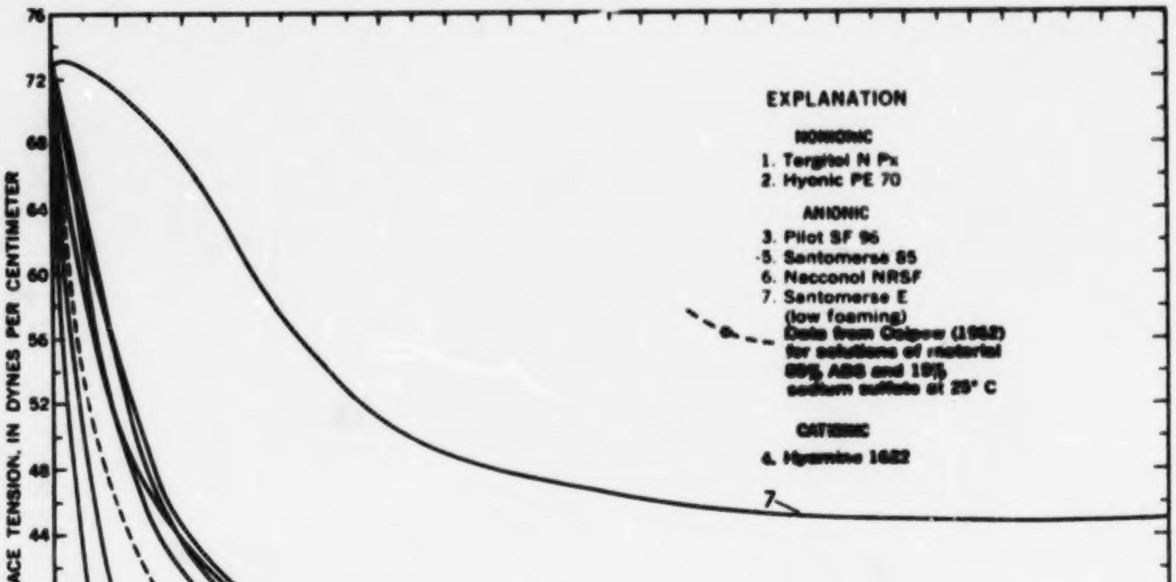


Figure 10. —Variation of surface tension with concentration for various surfactants at 20°C.

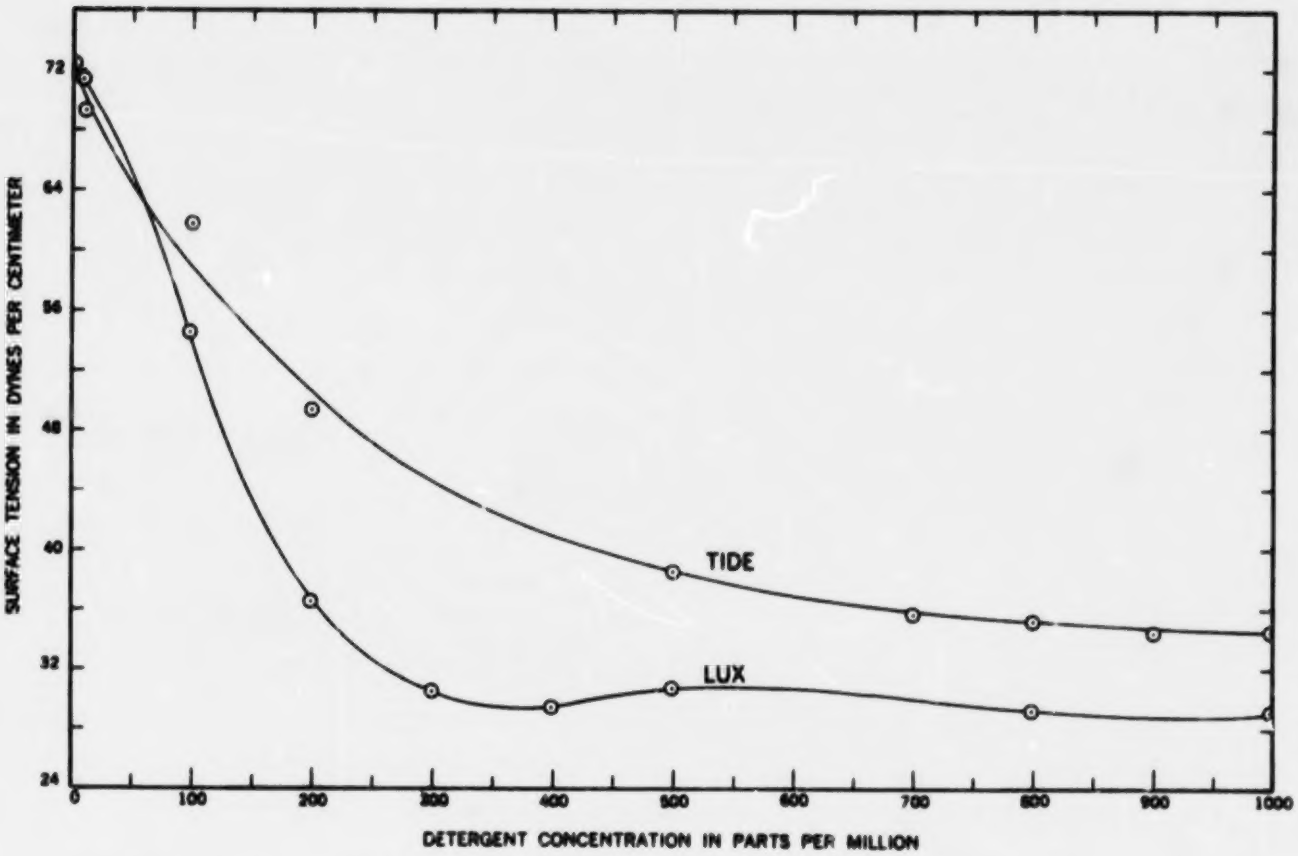


Figure 11. —Variation of surface tension of commercial detergents for different concentrations at 20°C.

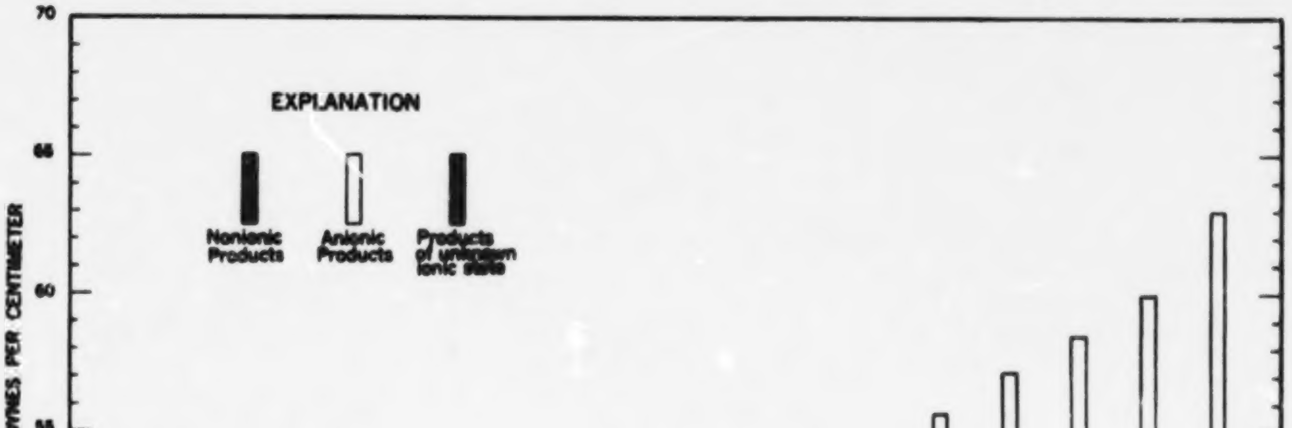


Figure 12. —Surface tension of solutions containing various commercial detergents at a concentration of 200 ppm (20°C, pH 7).

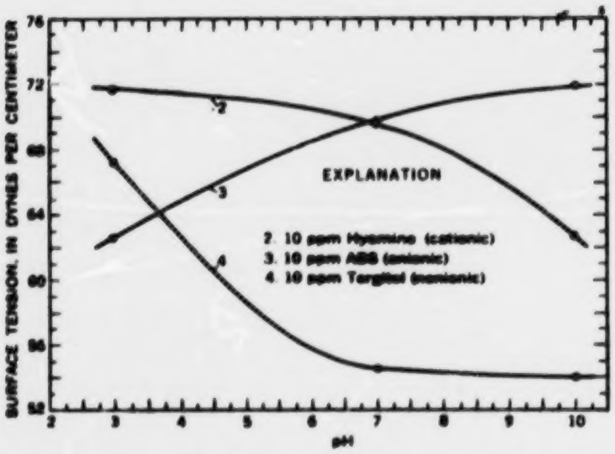


Figure 13.—Variation o surface tension of surfactant solutions at 20°C.

values probably reflects major variations in surfactant concentrations in these commercial detergents. The influence of pH on surface tension is shown in figure 13. In dilute solutions of anionic surfactants, surface tension increases with increase in pH, whereas in solutions of cationic and nonionic surfactants, surface tension decreases with increase in pH. With respect to anionic ABS, the presence of acid "builders" and basic "builders" in solution would tend to decrease and increase surface tension, respectively. Similar pH effects have been observed on aqueous soap solutions (Long and others, 1937). Electrolytes in dilute solutions of anionic surfactants produce additional lowering of surface tension at a specified concentration. Table 12 shows values of surface tension for solutions containing ABS with and without electrolytes. Surface tension can be lowered significantly even in dilute solution, 0.001 percent (10 ppm) of ABS with 100 to 300 ppm of salt in solution. The effect of lowering of surface tension with salt in surfactant solution has been observed by others (Powney and Addison, 1957; Harris, 1946, and Jones and Ray, 1937). Electrolytes in concentrated solutions (greater than 0.006N) are normally negatively adsorbed at interfaces and produce small increases in surface tension. However, electrolytes in dilute solution (less than 0.006N) can be positively adsorbed at interfaces and cause lowering of surface tension in addition to that produced from the surfactants alone like ABS.

Table 12.—*Surface tension values of aqueous solutions containing 85 percent ABS, 15 percent sulfate, and various amounts of electrolyte (Osipow, 1962, p. 148).*

Conc., percent	Distilled water	Surface tension at 25°C (dynes cm^{-1})	
		100 ppm electrolyte	300 ppm electrolyte
0.001	66.0	48.0	43.0
.01	38.0	32.0	28.0
.05	29.5	26.7	27.2
.10	28.6	26.8	27.4
.15	28.6	26.7	27.3
.20	28.9	26.7	27.4

The variation of surface tension with temperature can be shown in a number of ways. For a specified concentration, surface tension can be reasonably predicted from the empirical relation:

$$\gamma = \gamma_0 (1 - aT) \qquad (51)$$

γ_0 = surface tension at the lowest temperature

a = slope $\left(\frac{d\gamma}{dt}\right)$ of the surface tension - temperature plot

T = temperature (°C)

Data in figure 4 were used to show the change in surface tension with temperature for the range 2°C to 35°C. Figure 14 shows that the surface tension of ABS solutions decreases linearly with increase in temperature. At ABS concentrations of 10 ppm and 100 ppm, the slopes (a) are 0.17 and 0.19 dynes cm^{-1} T^{-1}, respectively. Only a small increase in slope was observed for a 10 fold increase in concentration.

Detailed studies on the effect of pressure upon surface tension are limited. It is commonly believed that high vapor pressure over the liquid tends to decrease surface tension because attraction of the surface molecules by those of the vapor would neutralize the inward attraction of the surface molecules, to a certain extent, and reduce surface tension (Adams, 1941, p. 168). In a recent study (Rice, 1947) it was shown that $\frac{\partial\gamma}{\partial P}$ (dynes cm^{-1} at.$^{-1}$) determined at 21°C for pressures up to 100 atmospheres on diethyl ether [$(C_2H_5)_2O$] and ethanol (C_2H_5OH) amounted to 0.02 when pressure was controlled by hydrogen, with the use of carbon dioxide on diethyl ether - $\frac{\partial\gamma}{\partial P}$ changed to 0.2 up to 10 atmospheres, suggesting that both the nature of the vapor and total vapor pressure significantly influence surface

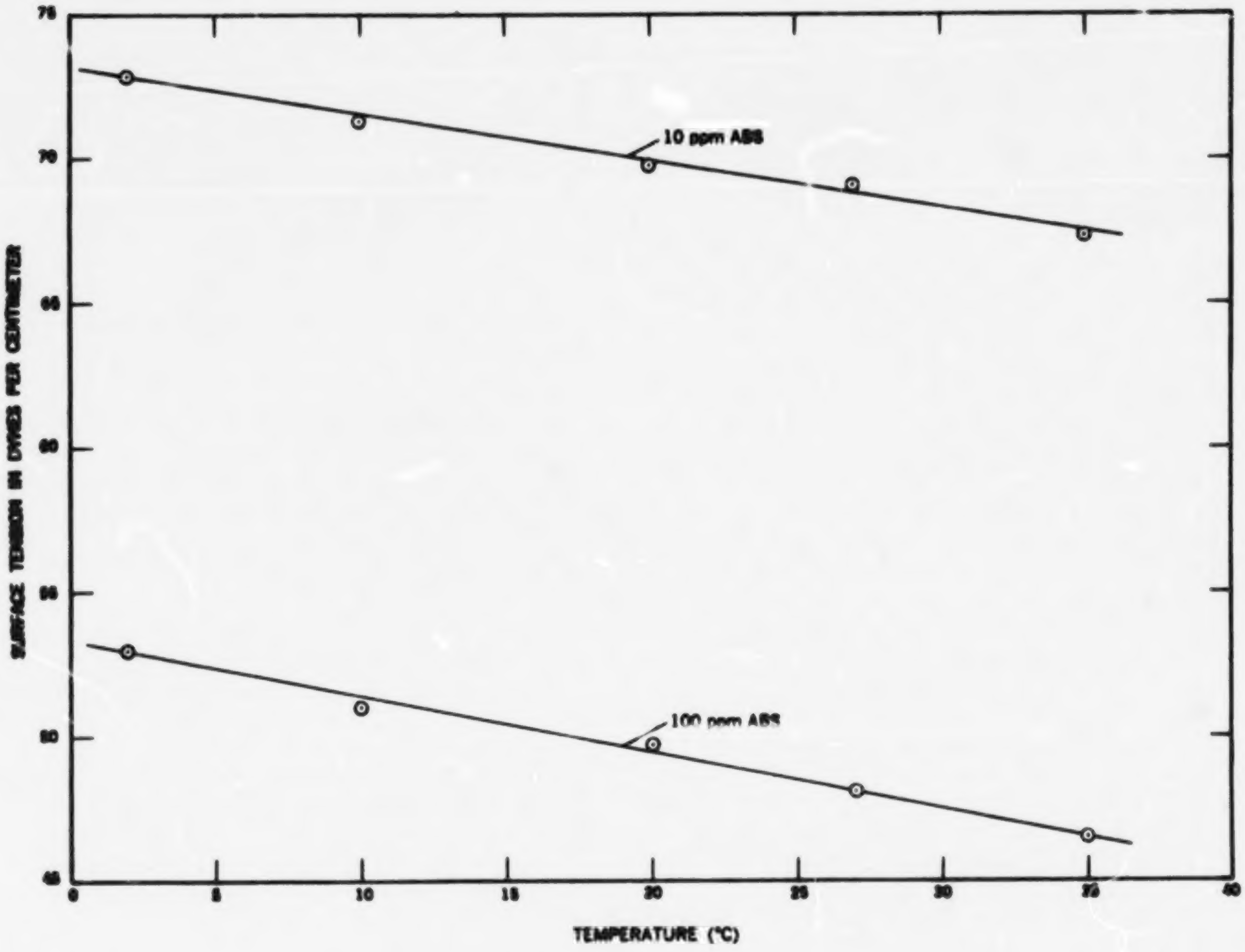


Figure 14.—Variation of surface tension of ABS solutions with temperature (2°C to 35°C).

tension. In pure one component systems, liquid $\rightleftharpoons$ vapor, surface tension would not change with pressure because of phase rule consideration; this condition does not exist in natural water.

Measurements on the surface tension of ABS in water indicated the following:

(1) At 20°C, ABS (10 ppm) has surface tension values slightly below that of pure water (72 dynes cm^{-1}). Surface tension is additionally increased and decreased below and above 20°C, respectively. If other surfactants are in solution with ABS, additional lowering of surface tension would be predicted; other surfactants (soap, proteins, and other organic products) may arise from discharge wastes or natural animal or vegetable decay.

(2) At a pH of 7, solutions containing 10 ppm of ABS have surface tension values slightly below that of pure water. In acid solution and basic solution of ABS with respect to pH 7, surface tension will be, respectively, decreased and increased from this value.

(3) If electrolytes (ionizable salts) are in dilute solutions of ABS, surface tension of the solution can be significantly lowered beyond the value produced from ABS alone (see Table 12).

Though the above data show that small concentrations (10 ppm) of ABS in natural water cannot significantly lower the surface tension below that of pure water, higher concentrations of ABS, other surfactants and salts in solution may influence this parameter.

SURFACE TENSION OF NATURAL WATER

In natural water or waste water, only limited data are available with regard to determinations of surface tension. The surface tension of sewage water at 25°C was studied for a three-year period at Indianapolis (Bowers, 1952). These values ranged from 38.9 to 71.6 dynes cm^{-1} with the bulk of values falling between values of 40 to 60. For total solids ranging from 500 to 1300 ppm, the respective surface tension values were 61.3 to 47 dynes cm^{-1}. Solutions containing dissolved solids (400 to 1000 ppm) produced surface tension values between 60.2 to 56.8. Solutions of suspended solids in the range 0 to 500 ppm gave surface tension values that ranged from 62.8 to 43.1. For both plain aeration and activated sludge, increase in dissolved oxygen between 0 to 6 ppm produced changes in surface tension that ranged from 52 to 62 dynes cm^{-1}. From Bowers' study the following conclusions may be deduced:

(1) surface tension decreases with increase in total solids, dissolved solids, and suspended solids.

(2) surface tension increases with increase in dissolved oxygen content and

(3) surfactants in solution, like ABS, probably influenced the lowering of surface tension of these solutions most directly.

In our study the surface tension of sewage effluent from the Denver sewage-treatment plant was determined at 20°C over a period of two years. These values ranged from 63 to 71.5 dynes cm^{-1}. Weekly determinations of certain constituents in the Denver plant effluent water had the following ranges: detergent (ABS), 3.0 to 7.5 ppm; bacteria (Escherichia coli), 150,000 to 250,000 per ml; dissolved solids, 750 to 1120 ppm; dissolved oxygen, 0.0 to 5.0 ppm; biochemical oxygen demand, 125 to 250 ppm; and pH, 6.2 to 8.1. Although a minor amount of the difference between the surface tension of sewage effluents at Denver and Indianapolis can be attributed to a difference in temperature of measurement (20°C at Denver and 25°C at Indianapolis), most of the difference probably is due to variation in composition of the sewage effluent at the two cities. The composition of a sewage effluent is influenced by waste disposal from industry, agriculture, and other sources. Because no two cities are likely to have sewage effluents of identical compositions, differences in surface tensions of their sewage effluents are to be expected. The wide range in variation of surface tension of the above sewage effluents probably results from differences in composition of the effluent from time to time.

In another study (Adam, 1937), the surface tension of sea water and estuaries was determined. The values ranged from about 52 to 72 but were reported without regard to temperature. From the study it was concluded that:

(1) Surface tension of the sea near the coast is nearly equal to that of pure water except near sewage outfalls or other sources of contamination.

(2) Creeks, small harbors, and confined areas of water may have their surface tension considerably lower than normal (5 to 10 dynes cm^{-1}).

(3) The surface tension of river surfaces depends more on their flow than on their transparency; some rapid, very muddy appearing streams have normal surface tension, while more sluggish, but clear streams or lakes may show considerably lower values. The values determined near a river bank are lower than more distant from this point; perhaps surfactants produced from organic decay of vegetation near the bank accounts for this observation.

In another study on natural water, over 100 determinations of surface tension were made on 40 lakes in northern and southern Wisconsin (Hardman, 1941). About 59 percent of the total determinations were equivalent to that of pure water at 25°C (72.0 dynes cm^{-1}), the remainder gave surface tension which could be correlated with the lake classification based upon its biological productivity. The values ranged as follows: Oligotrophic lakes, 70 to 72 dynes cm^{-1}; Eutrophic lakes, 52 to 72; Bog lakes, 52 to 72; Lakes with foam, 63 to 70; Near Lemna and lillies, 52 to 67; and during plankton bloom, 52 to 72. Certain chemical factors have been employed to interpret these observations. Near mud flats (anaerobic conditions) the generation of hydrogen sulfide, carbon dioxide and methane seemed to have little influence on surface tension. In certain areas, brown suspensoids in solution produced surface tension as low as 52 dynes cm^{-1}; this effect has been suggested to result from surfactants (tannins, glucosides, and saponins) derived from plants. Organic acids of low pH values in bogs also produced lowering of surface tension. The most important factors contributing to the lowering of surface tension in the lakes are attributed to biological activity. Eutrophic lakes containing high amounts of plankton or bloom have surface tensions as low as 52 dynes cm^{-1}. Lillies in lakes influence surface tension to the extent that values as low as 52 to 57 dynes cm^{-1} were observed in such areas. Likewise waxy plants also lowered surface tension. Physical factors in natural water have also been suggested as an influence on surface tension. Stagnant water containing significant amounts of biological activity have low values of surface tension because of the inability of the synthesized surfactants to be dispersed. Contrarywise, dynamic water in lakes had nearly normal values of surface tension because any surfactant produced via biological activity would not become concentrated enough to lower surface tension as a result of the physical mechanism of dispersion. Thus, natural water has variable degrees of surface tension; the values to be predicted depend upon biological activity, organic content, and local distribution as controlled by winds and currents.

SIGNIFICANCE OF SURFACE TENSION TO WATER POLLUTION STUDIES

The feasibility of removing pollutants by adsorption or ion exchange on solids in soil-gas-liquid environments depends on a complex set of conditions. If solids were completely saturated with a liquid phase (water), the possibility of adsorption would then be reduced to the characteristics at the solid-liquid interface. These characteristics may be influenced by (1) composition of the solid mineral, (2) bulk composition of the liquid, (3) surface area of the solid, (4) cross-sectional area of the solute, (5) crystalline nature of the solid and surface purity and geometry, and (6) electrical properties of both the solid and liquid. Although these characteristics seem complex, the complete situation has not been indicated. This situation (solid-liquid interface) merely represents one boundary condition (saturated zone) in soil-water environments. The other boundary condition is the solid-gas interface (unsaturated zone). Between these extremes, several degrees of contact between solids, liquids, and gases might be encountered. In a recent study (Stallman, 1963), the relations among these three phases have been presented with respect to: (1) increasing content of the wetting liquid, (2) increasing wetting liquid conductivity (3) decreasing content of gas phase or non-wetting liquid conductivity in the pore space. These relations are shown in figure 15. A similar analogy of the nature of water in soil has been presented elsewhere (Polubarinov-Kochina, 1962, p. 8). Figure 15A represents a static condition between solid and gas, which might exist in the unsaturated zone or more impermeable types of saturated environments (clay lenses in sandy aquifers). The transition from 15A to 15B represents films formed from reactions between solids and gases (or vapors); solids may be represented by any natural mineral and vapors by air, water, carbon dioxide, and others. Certain considerations between solids and gases have been

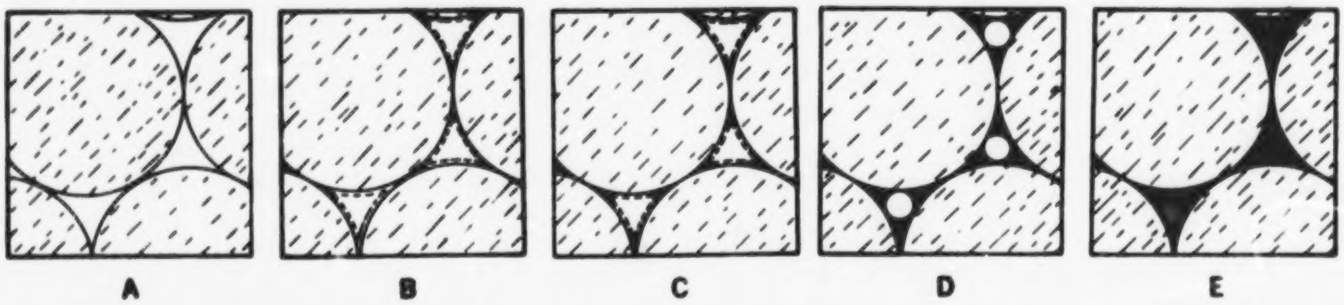


Figure 15.—States of liquids and gases in soil environment. A, shows gas or vapor (white) in contact with a solid (corss-hatched). B, shows the beginning of formation of a liquid film by gas condensation on solid. Outward from the solid (cross-hatched) the sequence would be a then liquid film followed by the gas or vapor (white). C, shows a more advanced condition of liquid film formation. The dark areas represent increase in amoumt of liquid from a film to a discrete drop. D, shows the liquid (black) has completely wetted the solid (cross-hatched with remnant gas (white) within the liquid. E, shows complete wetting of the solid by liquid. The gas has been completed replaced by liquid.

considered previously (Wayman, 1963C). This transition can be represented by

$$\underset{(15A)}{\text{Solid + gas}} \rightarrow \underset{(15B)}{\text{solid + liquid film}} \quad (52)$$

The simplest way to achieve gaseous adsorption on solids is through physical adsorption. Physical adsorption can occur at the solid-gas interface without being specific and at relatively low heats of adsorption (usually less than 10 kcal/mole); i.e. adsorption depends only upon the condensability of the gas to a liquid. Chemisorption is much more complex; both the chemical properties of the gas and solid are involved, the adsorption being specific and usually occurring at heats of adsorption greater than 10 kcal/mole. If physical adsorption dominates in the solid-gas interfacial environment, liquid films of water can easily form on solids when warm gases of the soil air permeates through cooler parts of the soil. As an example, the saturated vapor pressure of water is 23–37 mm Hg at 20°C and 8.72 mm Hg at 5°C; air saturated at 20°C would yield liquid water at 5°C until the lower vapor pressure were established. For CO_2, the same type of reasoning is valid, at least to temperatures of 31°C, the critical temperature of CO_2. In soils containing clays or finely divided solids (unsaturated conditions), liquid flow may be controlled by movement of moisture films. It is also significant to indicate that moisture may be tenaciously retained on clays under these conditions. Figures 15C–15E would seem to be most pertinent to water pollution studies because of the direct association of the wetting liquid upon a solid. The ability of a liquid to wet a solid is important for two reasons:

(1) adsorption of solutes contained in liquids would be extremely difficult without a significant amount of contact (wetting) between the solid and liquid and

(2) flow of liquid between fine-grained pores also demands a certain amount of contact between solids and liquids.

The phenomenon of wetting must at least be considered in water pollution studies. In natural systems, solids (minerals) previously wetted by air must be replaced by a liquid. Under equilibrium conditions, the three phases may be represented as shown in figure 16. Under equilibrium conditions, the sum of all the forces at the origin (0) must be zero or

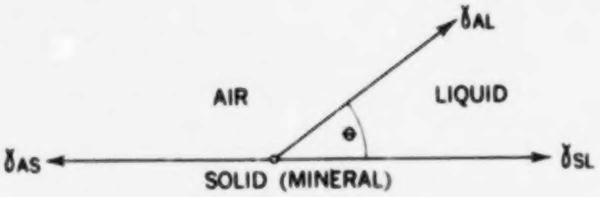


Figure 16.—Resolution of the three-phase surface force.

$$\gamma_{AL} + \gamma_{AS} + \gamma_{SL} = 0 \quad (54)$$

γ_{AL} = tension at the air-solution interface

γ_{AS} = tension at the air-solid interface

γ_{SL} = tension at the solid-liquid interface

θ = contact angle as measured across the liquid phase between the liquid and solid surfaces.

Rarely are the conditions in (54) attained but most interfacial phenomena may be represented in such systems. In natural systems, adsorption of solutes at interfaces or movement between pores, both involving wetting, requires that liquid replace the air adsorbed on the solid. This condition can be respresented in terms of work of adhesion at the liquid-solid interface (W_{SL}).

$$W_{SL} = \gamma_{AL} + \gamma_{AS} - \gamma_{SL} \quad (55)$$

For contact angles between 0 and 180°, equation (55) may be combined with the Young equation

$$\gamma_{AS} = \gamma_{SL} + \gamma_{AL} \cos\theta \quad (56)$$

to give

$$W_{SL} = \gamma_{AL}(1 + \cos\theta) \quad (57)$$

This latter equation is significant because W_{SL} may be evaluated in terms of measurable parameters γ_{AL} and the contact angle ($\cos\theta$). For $\theta = 0°$ and $\theta = 180°$, the solid would be wetted completely by water and air, respectively. Contact angles usually range between these values. If surfactants like ABS are in the liquid phase, γ_{AL}, γ_{SL} and γ_{AS} are reduced. Lowering the tension of γ_{SL} (see 55) increases W_{SL} and would permit air to replace liquid on the solid with great difficulty; however, if γ_{AL} is decreased, W_{SL} becomes lowered and air replaces liquid more easily on the surface. Thus, liquid can replace air (to effect wetting) more easily if surfactants are adsorbed at the solid-liquid as compared to the air-liquid interface. After liquid has been adsorbed on a solid by its replacement of air, the actual spreading of the liquid on the solid is governed by the free energy of spreading S_F or

$$S_F = \gamma_{AS} - \gamma_{AL} - \gamma_{SL} \qquad (58)$$

the spontaneous spreading of a liquid demands that $S_F > 0$. Thus adsorption of surfactant at both the air-liquid and solid-liquid interfaces (which normally occurs) would produce an increase in S_F and favor spreading. In this study surfactants in solution gave surface tension values significantly below that of water, which should aid in the wetting of solids and enhance adsorption on solids and movement through porous solids. In a previous study (Plegat, 1961) it was pointed out that water containing a cc per liter considerably increased water discharge in sands and decreased it in clayey sands treated in the laboratory or the field. The difference in these effects were attributed to the influence of capillarity on the displacement of liquids between mineral particles. If the spaces between particles are large, the surface tension impairing the flow by gravity is decreased by the detergent; fine-grained samples (small spaces between pores) capillary flow is decreased. The effects observed in coarse sands are understandable from surface tension effects alone and those found in fine capillaries might be explainable as shown below. One of the most reasonable equations for prediction of flow in fine pores is the Rideal-Washburn equation

$$\ell^2 = \frac{\gamma a t \cos\theta}{2n} \qquad (59)$$

where ℓ = rate of penetration of liquid in pores of uniform diameter

a = pore radius

t = a tortuosity factor

n = viscosity

Addition of surfactants would tend to lower surface tension and increase $\cos\theta$. As the size of openings between grains become smaller, the rate of liquid penetration is reduced, as observed by Plegat. However, to determine the effect of change in surface tension on liquid penetration, the evaluation of

$$\frac{\gamma a \cos\theta}{2n}$$

is required. Surface tension is a dynamic entity in water movement and should be given more serious consideration in flow studies.

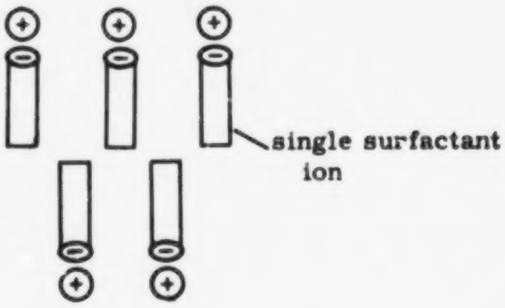
It can be concluded from data presented in this section that:

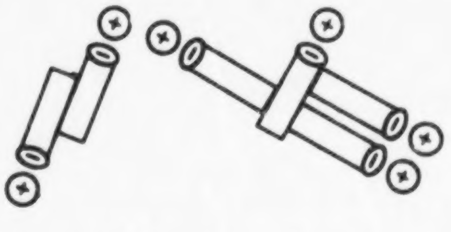
(1) surfactants in solution may alter the rate of flow of water in both coarse and fine-grained sediments and

(2) wetting phenomena that should influence adsorption from solution can depend in large part upon surface tension of solution.

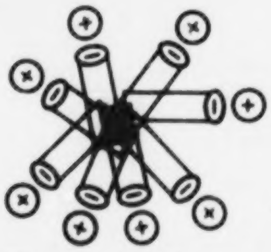
Critical Micelle Concentration (CMC)

Critical micelle concentration is that concentration of surfactant at which single surfactant ions in solution tend to form ionic agregates (micelles). Actually micelle formation may occur at concentrations below this critical value but present analytical methods cannot measure this type of reduced aggregation. For aggregation below the normal critical micelle concentration, the formation and suggested shapes of micelles may assume the form given below (McBain and McHan, 1948):

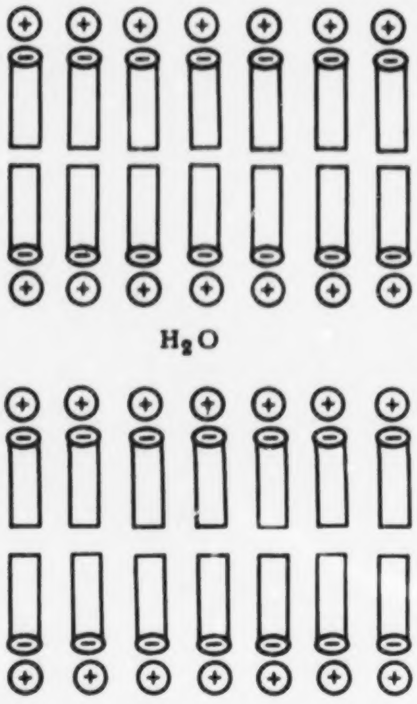



Shapes of micellar aggregates for conditions under the normal critical micelle concentration

have been suggested to be either spherical (Hartley, 1936)



or lamellar (Brady, 1949):



To indicate the impressive size of micellar aggregates, the molecular weights and micellar molecular weights of surfactants can be compared. Sodium branched dodecylbenzenesulfonate has a molecular weight of 361; the micellar aggregate of this compound contains 3 to 5 mols per micelle with a micellar molecular weight of 1000 to 1700 (Mankowich, 1954). Sodium-3-dodecylbenzenesulfonate and sodium-4-dodecylbenzenesulfonate contain 57 and 24 moles per micelle and have micellar molecular weights of 20,000 and 8,000, respectively (Ludlum, 1956). Table 14 shows the effect of electrolyte type on micellar molecular weight. The greatest effect seems to be associated with sodium sulfate.

The effect of change in micellar charge below the CMC with increase in surfactant concentration has not been investigated for ABS surfactants. For sodium laurate (NaL) the formation of a 1-1 electrolyte has been observed below the CMC (Ekwall and Lindblad, 1941). As concentration is increased for this compound, the formation of different ions with varied charge have been suggested (Ekwall and Lundblad, 1941; and Goette, 1949) as shown in Table 15. Such data might be significant to removal of ABS through adsorptive processes. If ABS behaves similar to sodium laurate and, if ABS forms micelles (small micelles) below the CMC, then the more highly charged the anionic aggregate becomes the greater becomes the tendency for its repulsion at a similarly charged solid mineral surface.

Table 13.—*Effect of electrolytes on the number of aggregates in the micelle for dodecylbenzenesulfonate at 25°C. (Mankowich, 1955).*

Electrolyte	Concentration (percent)	Number of aggregates in sodium dodecylbenzenesulfonate
None	-----------	5
$Na_2PO_4.H_2O$	0.6	60
	.9	74
	1.5	148
	2.0	248
Na_2SO_4	.3	53
	.6	64
	.9	59
	1.5	210
	2.0	371
$Na_5P_3O_{10}$	.3	51
	.6	67
	.9	68
	1.5	74
	2.0	83

Table 14.—*Relationship of sodium laurate concentration to micellar charge, small micellar charge, and type of ionic aggregate.*

Na laurate concentration (molarity x 10^3)	Charges on laurate anion	Type multivalent ion
0–6	1	L.HL
6–21	2	NaL.HL
21–28 (CMC)	4	3NaL.HL
28–37	6	--------------

The CMC can be influenced by a number of variables.

Increase in temperature is believed to increase the CMC. For sodium dodecyl sulfate in water, the CMC decreases between 10°C and 20°C; between 20°C and 35°C remains essentially constant; and then rapidly increases with increase in temperature (Flockhart, 1957). Similar data on ABS are not presently available.

Change in CMC with increase in chain length for a homologous series can be represented by (Evans, 1956; and Klevens, 1952):

$$\log \text{CMC} = A - BN \tag{60}$$

where N is the number of carbon atoms in the chain

B is empirical constant (log 2)

A is a constant dependent on temperature and homologous series determined from a known value of CMC for one member of the series.

For ABS, the benzene ring is equivalent to 3.5 carbon atoms in its effect on the CMC (Paquette and others, 1943); if "builders" are in solution with ABS, the CMC can be represented by (Ginn and others, 1959):

$$\text{CMC} = 0.00425 - 0.00156 \log \left[\frac{\text{Na}^+ \text{ builder}}{\text{Na}^+ \text{ active}}\right] \tag{61}$$

This effect (61) is attributed to a sodium or common ion effect. For nonionic surfactants the following relation holds (Hsiao and others, 1956):

$$\ln \text{CMC} = 0.056\,R + 3.87 \tag{62}$$

where CMC is in micromolar units

R represents the mol. ratio of ethylene oxide to phenol.

If ionic salts (electrolytes) are in solution the CMC of pure ionic surfactants is lowered. This effect depends only upon the concentration of ions of opposite charge to that of the surfactant. For anionic ABS, cations in solution become the significant entity. The valence of the cation follows the Schulze-Hardy rule; that is the higher the valency of the cation, the smaller is the amount of electrolyte required for lowering the CMC (Lange, 1951; and Powney and Addison, 1937). If "builders" are in solution with ABS, "builder" anions also influence the lowering of CMC in the order (Ginn and others, 1959): OH^{-1}, CO_3^{-2}, PO_4^{-3}, $P_2O_7^{-4}$, $P_3O_{10}^{-5}$.

The location of the hydrophilic group may also influence the lowering of the CMC. Studies on alkyl sulfates (Dreger and others, 1944) show that the attachment of the sulfate group at the middle of the chain will produce a 2.5-fold decrease by addition of one carbon atom to each end of the chain. Similar studies on ABS are not available.

The determination of the CMC on essentially pure solutions of ABS seems to vary with the method of determination. By employing a dialysis technique at 25°C, the CMC of sodium dodecylbenzenesulfonate was determined as 420 ppm (Wright and others, 1939). In another study (Ginn and Harris, 1958) found values of CMC for sodium dodecylbenzenesulfonate as 400, 1530, and 1230 ppm for the spectral dye photometric, conductivity, and surface tension methods, respectively. Other values mentioned in the literature indicate CMC values for ABS that range from 300 to 1530 ppm. One of the writers (Wayman, 1963b) employed the maximum bubble pressure method (surface tension) and determined the CMC of a 99 percent pure branched chain ABS as 1000 ppm.

Significance of CMC to water pollution studies

The CMC is the most significant surfactant property influencing surface activity. At this concentration the surfactant is operating essentially at its maximum effect. With regard to natural water systems involving adsorption of surfactants on solid minerals, the surface-activity at the solid-liquid interface should produce its maximum effect at the CMC. Two practical situations may arise in this consideration:

(1) The net charge on the micelle probably exceeds that on a single surfactant ion. For ABS micelles this net charge is negative. In solution clays are normally charged negatively except in acid media. At pH 7 and at the CMC, surface activity at the solid-solution interface should be at its maximum effect; however, because of the highly charged negative solute (ABS) and a negatively charged mineral surface, adsorption should be reduced because of repulsion. In acid solution under the same conditions the clay surface becomes more positively charged and adsorption of the

surfactant micelle should be enhanced because of attraction.

(2) Because of the law of mass action and Coulomb's law, surfactant micelles containing a specified surface charge should attract ions of opposite charge to produce electro-neutrality. For an ABS micelle (negatively) charged with attached cations, the adsorption on clay surfaces should occur most readily at pH 7 and above. In acid solution the increased number of positive sites on the clay surface should inhibit or reduce adsorption.

It is not possible to determine whether true micelles actually form from the small concentration of surfactants in natural water. However, increased surface activity from formation of smaller micelles cannot be ruled out. The likelihood of either (1) or (2) above in natural solution to effect ABS adsorption on clays or other mineral surfaces will be discussed in a subsequent section on adsorption.

Foaming

Foams created in water and sewage treatment processes from surfactants have been one of the aesthetically distasteful by-products resulting from either incomplete degradation of these substances by bacteria, or their synthesis by bacteria or vegetation in water. However, foaming in water is not entirely indicative of synthetic detergents (ABS-like surfactants) alone. Foams may also arise from soap, saponins, proteins, or from surfactants produced by biological degradation from enzymes and bacteria. Certain studies (Rohlich and Polkowski, 1957) indicate that when both ABS and degraded proteins are in solution a marked increase in foam volume and stability was observed as compared to foams formed by each separately. Although foaming in water has been attributed to an increase in usage of synthetic detergents, this phenomenon was actually observed in aeration tanks in a sewage plant as far back as 1932, prior to the manufacture of synthetic detergents (Martin, 1954).

Foaming in water and sewage plants has been common knowledge since about 1950. Because these problems have increased in intensity from this date, it must be recognized that synthetic detergents have at least contributed their part. In sewage operation foaming is believed to be reduced or eliminated if certain concentrations of mixed liquor solids are available to adsorb surfactants from solutions (Hoot, 1954; Greeley, 1953; and Wells and Scherer, 1952), in natural water (rivers and streams), concentrations of suspended solids seem to be below that required to eliminate adsorption of surfactants in prevention of foaming. It is also significant to indicate that suspended sediments are inefficient in removal of ABS from solution; these detailed aspects of adsorption of ABS on natural materials will be presented in a different section of the report.

Foams may be created whenever a gas flows through a liquid containing surfactants. The stability of foams results from the persistence of bubbles in the surface at the air-solution interface. As bubbles move through the liquid, attached surfactant is transported to the surface. Certain aspects of bubble movement through surfactant solutions have been given elsewhere (Fuerstenau and Wayman, 1958); the general mode of surfactant transport from solution to the surface involves the projection of the hydrocarbon chain into the bubble with the polar group projecting into the solution. The activity of a foam involves growth of small bubbles at its base with subsequent coalescence into large bubbles at the top of the foam with eventual decay; the transition from smaller to larger bubbles in the foam cross-section can be explained in part from gaseous diffusion between a state of high pressure (small bubbles) to one of lower pressure (large bubbles). The stability (life) and foam volume of a foam depends on several factors:

(1) the concentration and type of the surfactants

(2) presence of electrolytes

(3) availability and type of gas

(4) pH

(5) temperature.

In natural water the concentration of surfactants in the bulk solution may range from hundredths of a part per million to several parts per million; however, if such water is subject to foaming, the surfactant concentration (foam) may approach several hundred to a thousand or more parts per million. Not only are foams undesirable but contact of such substances with vegetation may cause deleterious effects. Because limited, published data are available on foaming characteristics of anionic, cationic, or nonionic surfactants, certain foaming aspects of these substances were determined. Previous work (Sawyer and Fowkes, 1958) indicates the susceptibility of stable foam formation in the order: (1) branched ABS, (2) n-ABS, (3) sec-alkylsulfates, (4) 2-n-alkanesulfonates, and (5) primary alkyl sulfates; it is also indicated that the addition of nonionic surfactants enhances foam stability. In another study (Peper, 1958) foams produced from solutions containing 1000 ppm of ABS became stabilized with as low as 2.0 ppm of $CaCl_2$ or with 2.0 ppm of $CaCl_2$ plus 20 ppm of the fatty acids (sodium laurate or sodium oleate); unstable foams of ABS were obtained with 2.0 ppm of $CaCl_2$ plus 20 ppm of the soaps sodium palmitate of sodium stearate. The present study was undertaken to evaluate the effects of concentration, surfactant type, pH, temperature, builders, and bacteria on the formation of foam.

Figure 17 shows the apparatus (Wayman and others, 1962d) employed to study foaming characteristics of various surfactant solutions. The unit consists of a large chromatographic solumn (outside diameter, 5.8 cm., and length, 30.0 cm., graduated to 0.5 cm.) connected to a lower tube (outside diameter, 1.0 cm., and length, 18.5 cm.) by a 55/35 tube-socket ground-glass joint; a coarse-porosity fritted disc is sealed to the upper end of the lower tube.

The apparatus can be operated by releasing air at a constant flow rate into a solution containing a surfactant in the chromatographic column, and observing the height (or volume) of foam formation as a function of time. The portion of the apparatus containing the liquid can be immersed in a constant temperature both to evaluate the influence of temperature on these characteristics. Table 15 shows the rate at which a solution containing 1000 ppm of ABS foams at different flow rates at 20°C. The foam height varies directly with the flow-rate of air.

Figure 18 shows the influence of concentration on amount of foam formation at 20°C and air flow-rate of 720 cc per minute for different commerical surfactants. The

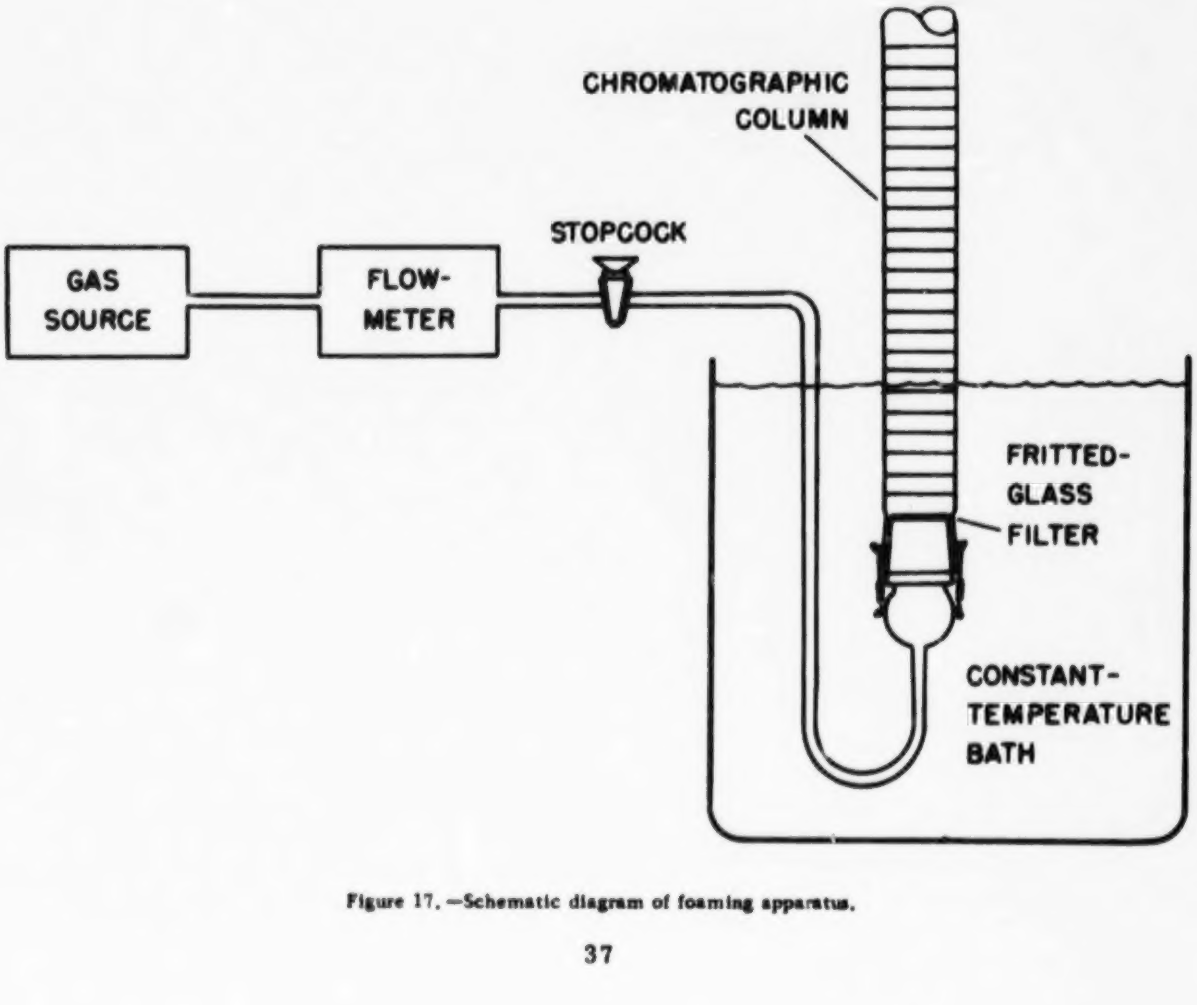


Figure 17. —Schematic diagram of foaming apparatus.

Table 15.—*Variation of foam height with changes in flow-rate of gas and in time*

Time (sec.)	Foam height (cm) at indicated flow-rate	
	280 cc air per minute	720 cc air per minute
20	4.5	10.0
50	10.0	26.0
100	21.0	54.0

respective anionic surfactants and their ABS concentrations were:

Santomerse E (low foaming): 70 percent
Santomerse 85: 85 percent
Nacconol NRSF: 92 percent
Pilot SF 96: 96 percent

Hyamine 1622 is a 50 percent solution of a cationic surfactant. Tergitol NPX is a 100 percent nonionic surfactant. The Hyonic series represent nonionic surfactants with varying hydrophobic nature and, therefore, water solubility increases with number. For example, Hyonic PE 70 exemplifies a surfactant with 70 percent hydrophobic to 30 percent hydrophilic character. Santomerse E shows a poor tendency to foam because of its relatively short alkyl chain, which produces a reduction in surfactancy properties. The cationic surfactant tested foams to a lesser degree than anionic or nonionic surfactants. Anionic and nonionic surfactants foam nearly equally well. Both anionic and nonionic surfactants will not produce measurable, stable foams below about 2 ppm; these data seem to conflict with the popular belief that ABS foams vigorously at 0.5 ppm. *This finding contains a certain amount of speculative data for reasoning regarding foaming in natural water.* If the purported average ABS content of natural water is below 2 ppm, the amount and intensity of foam must be explained in terms of surfactants in solution and in addition to ABS. The minimum foaming concentration of the cationic surfactant was about 8 ppm.

Foam stability was studied by observing the amount of time required for a column of foam 56 cm high to decay to 0.3 cm. Figure 19 (Wayman and others, 1962e) shows that foams from anionic and nonionic types are more stable than the one cationic tested at 20°C. Foam stability of anionic surfactants increases as the ratio of hydrophobic to

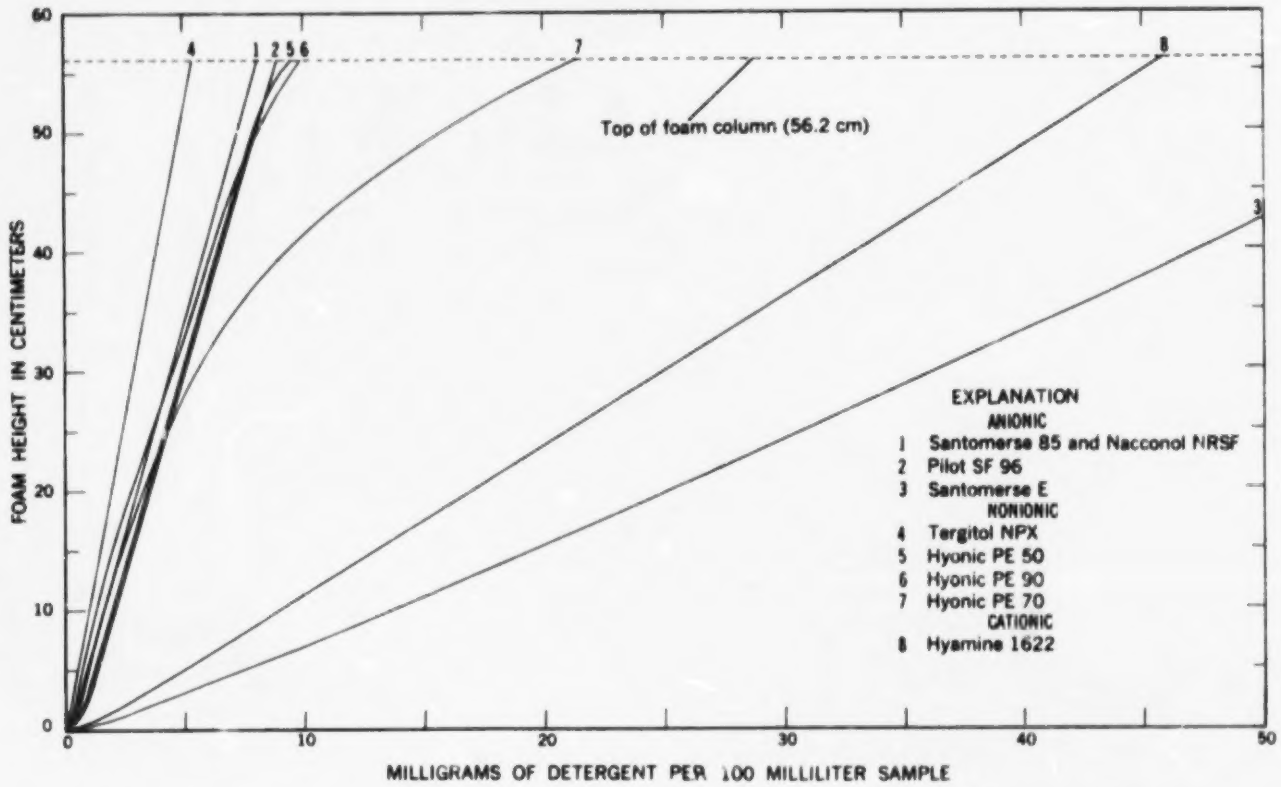


Figure 18.—Variation in foam height with surfactant concentration at 20°C and flow rate of 720 cc per minute.

hydrophilic groups of the molecule increases.

If cationic surfactants are in solution with anionic types, foaming may be eliminated. Figure 20 shows the foaming characteristics of dilute solutions of both cationic and anionic surfactants. As little as 10 ppm of the cationic surfactant can eliminate foaming of ABS solutions containing as much as 40 ppm and reduces the amount of foam in more concentrated ABS solutions. This effect can be attributed to the interaction of the cationic and anionic surfactant as indicated by the formation of a white precipitate. Similar observations on cationic-anionic surfactant interactions have also been made by Samples (1962). Thus, cationic surfactants behave like foam depressants for ABS.

The influence of temperature on foaming is shown in Figure 21. For solutions containing 10 ppm of ABS, a greater amount of foam is formed at 20°C than at 10°C. Although the rate of formation is greater at 20°C than at 10°C, the overall decay ratio of the two foams are similar. The temperature effect can most readily be explained on the basis of surface tension. At a specified concentration, surface tension is lowered as temperature

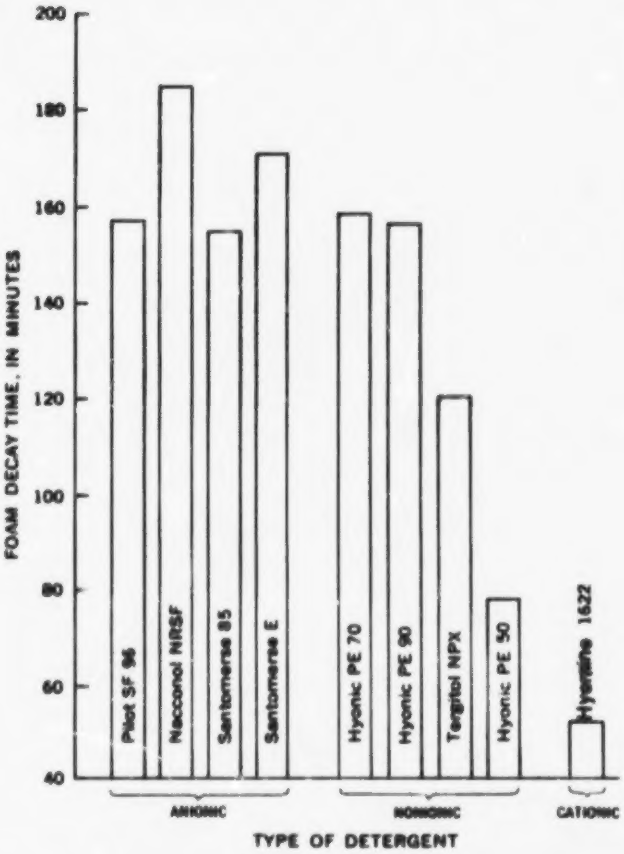


Figure 19. —Time required for a column of foam 56 cm high to decay to 0.3 cm for various anionic, nonionic, and cationic surfactants.

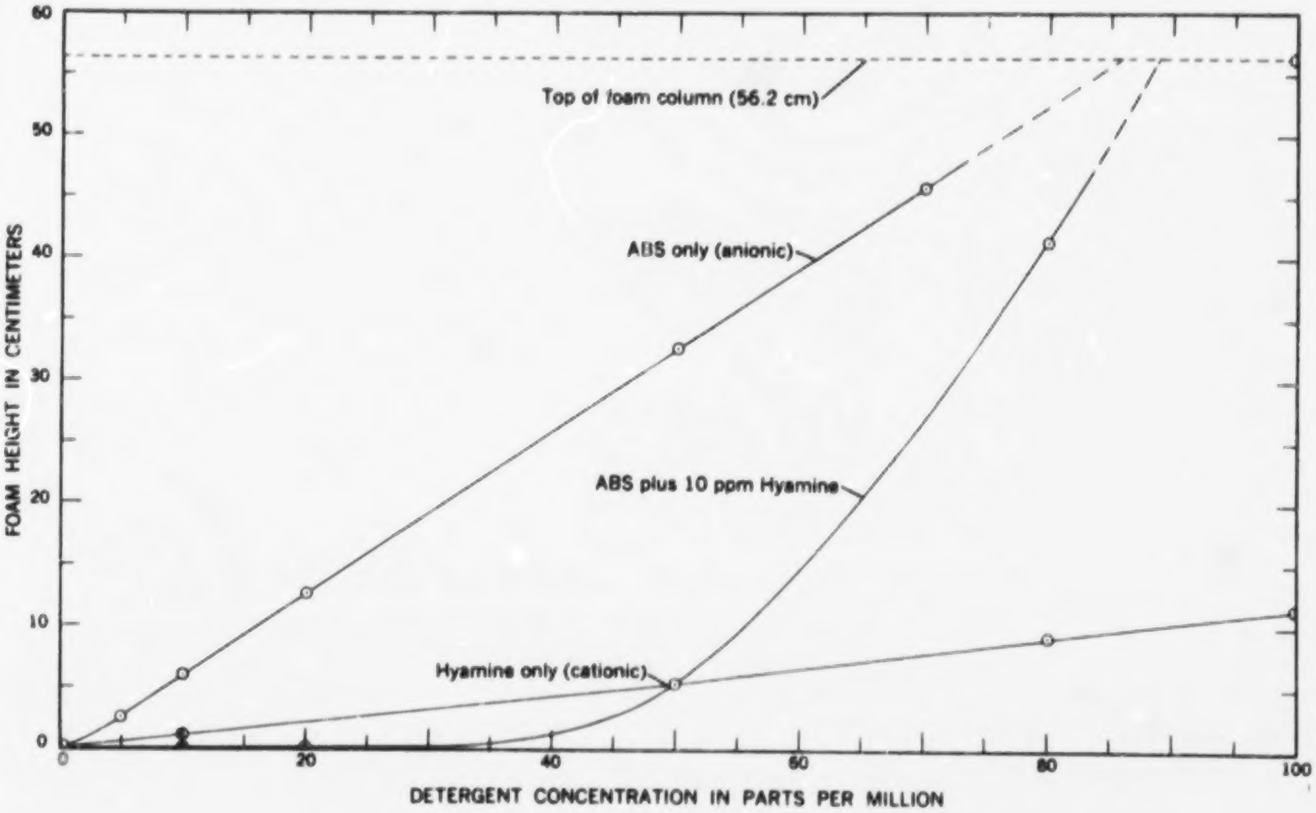


Figure 20. —Effect of cationic surfactants on the foaming of ABS solutions.

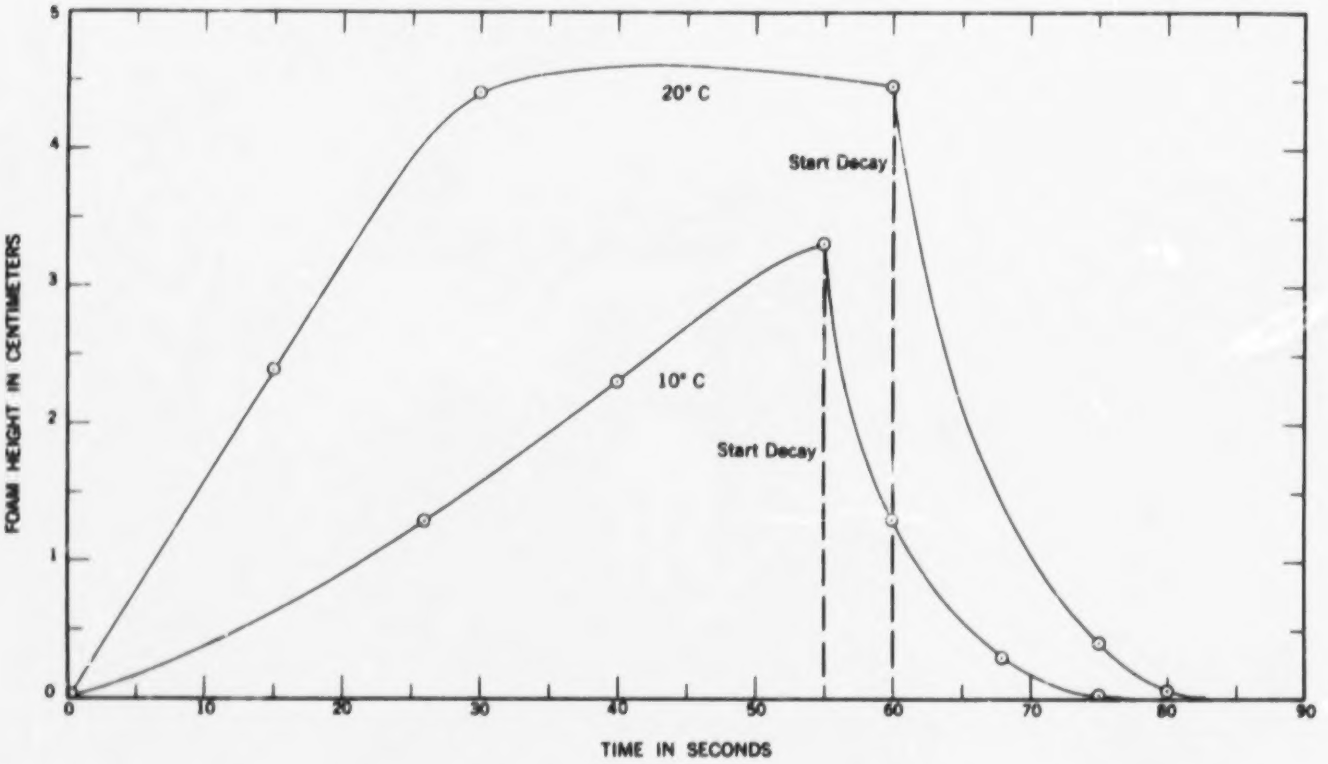


Figure 21. —Influence of temperature on foaming in dilute ABS solutions.

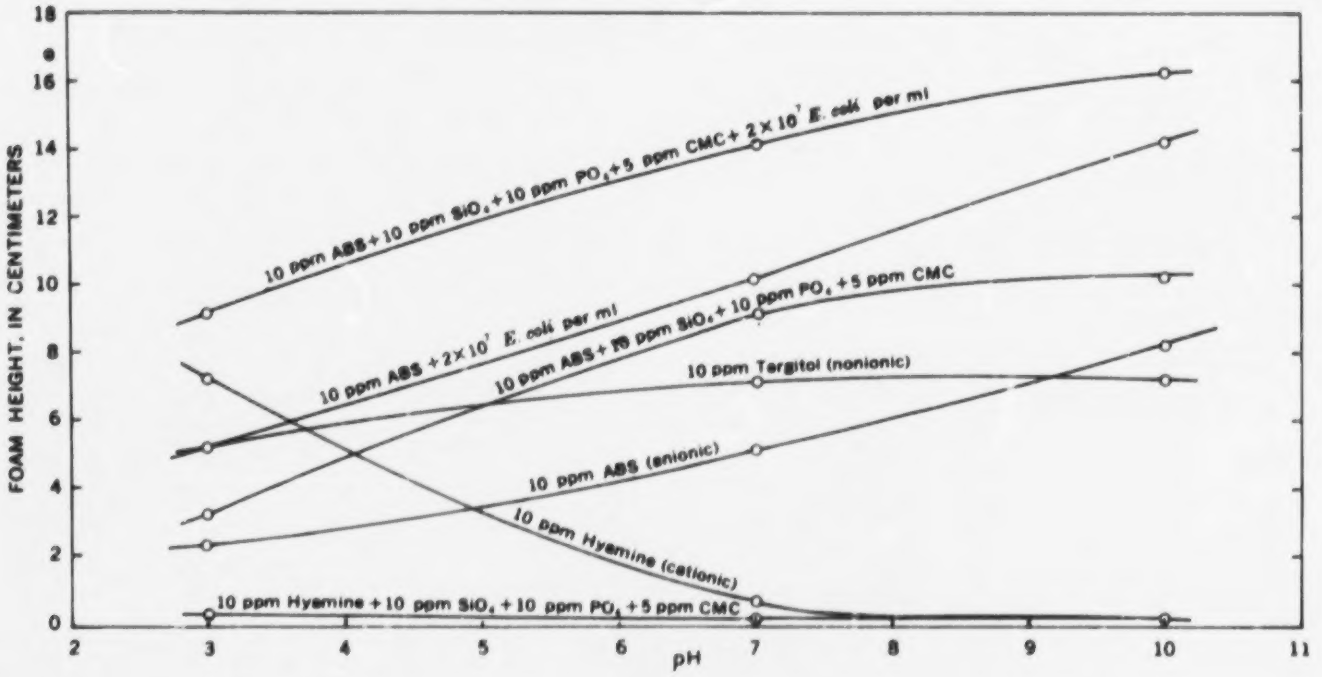


Figure 22. —Influence of pH, builders, and bacteria on foam height for various surfactants.

increases (Figure 14). Because surface tension is one of the parameters responsible for foaming, these observations are readily explainable. It is also important to indicate the relative degree of instability of these dilute water foams. The stability of ABS foams in natural water no doubt depends on other surfactants or inorganic salts in solution.

The influence of pH, anionic builders (silicate, phosphate, and carboxymethylcellulose), and bacteria on foaming is shown in Figure 22.

Anionic ABS solutions foam more profusely with increase in pH between 3 and 10; the foaming of cationic surfactants decrease with increase in pH.

Foaming of nonionic surfactant solutions are essentially uninfluenced by changes in pH. From these effects of pH, certain hydrolytic phenomena must occur at the air-solution interface as a function of pH. What these effects are, were not studied in sufficient detail to deduce valid reasons. Anionic builders (silicate, phosphate, and carboxymethylcellulose) in solution with ABS enhance foaming and also stabilize ABS foams; when these substances are in solution with cationic surfactants foaming is depressed or eliminated because of the interaction of the cationic surfactant with some substances.

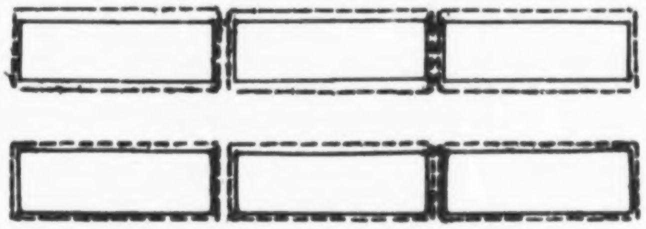
This study indicates that water supplies tapping ground water aquifers should not foam vigorously at ABS concentrations of less than 2.0 ppm, if ABS is the only surfactant present.

The stability of foams in natural water is influenced by several variables. Foams are more stable at lower temperatures. Foams are relatively unstable at concentrations of less than 2.0 ppm but may foam at lower concentrations if other organic surfactants such as soaps or proteinaceous material are in solution. The types of surfactants most common in natural water probably contribute more readily to foaming in the pH range from 7 to 10. Escherichia coli in water enhances the tendency to foam. Small concentrations of cationic surfactants or other antifoaming compounds may reduce or destroy foaming produced from the anionic surfactant, ABS.

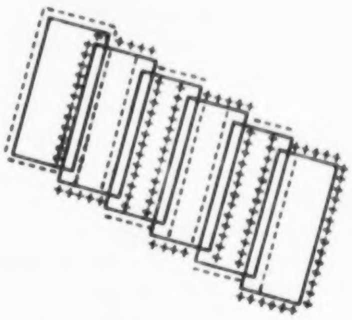
Dispersion, Flocculation, and Viscosity of Solutions Containing Surfactants

Experiments with detergent solutions have suggested that detergent components are very important in flocculating and dispersing clays and therefore have a direct relation to the viscosity of clay-water suspensions. Viscosity in turn is a controlling factor in the velocity of the flow of fluids. In heavily loaded streams or rivers, the movement of particles including water may be controlled by such phenomena (dispersion and flocculation). Much of the following discussion pertains essentially to surface water; viscous effects from flocculation and dispersion by infiltration of water into the ground are probably nil because of the filtering action of soils except, possibly, in coarse sub-surface glacial gravels.

The theory of dispersion and flocculation, although readily interpretative, is complex in solid-water-solute systems. In simplified form, a dispersed system of suspended solids results from the repulsion of particles containing like charges as shown below:



This system represents particles surrounded by like negative charges to effect repulsion (dispersed system). In contrast to such a system (flocculated) particles surrounded by unlike charges attract each other and become flocculated such as shown below:



The behavior of these two systems with respect to viscosity are diversely different. Dispersed systems would tend to move with water without serious resistance to flow (low viscosity) whereas flocculated systems would tend to offer resistance to flow (increase viscosity).

Whether or not dispersion or flocculation will occur in solution depends on the properties prevalent at the solid-solution interface. These properties would normally be controlled by composition of the solid and concentration and type of ionic solutes in solution. In addition to the above effects, dispersion and flocculation can be influenced by the extreme anisometric shape of the particles, especially for clays (van Olphen, 1963). Plate like clay particles have two distinct and different crystallographic surfaces, the flat face surface and the edge surface. Plate like particles may become flocculated in three different ways:

(1) face to face—leads to thicker plates

(2) face to edge and

(3) edge to edge

where both (2) and (3) lead to large voluminous flocs or gels. Edge to face flocculation may be conditioned through attraction of oppositely charged particles. In direct contrast, edge to face dispersion may be prevented or reduced by adsorption of anions on surfaces to cause particle repulsion.

Effects of ionic solutes on dispersion or flocculation are multifaceted. Normally clay minerals possess a net negative charge on their surfaces. This net charge normally results from isomorphous replacement, dissociation of hydroxyl groups, or anionic adsorption.

Isomorphous replacement occurs by ions of lower valency substituting in the crystalline lattice. For example Mg^{+2} substituting for Al^{+3} or Al^{+3} substituting for Si^{+4} leaving a residual lack of cations which is reflected on the clay surface as a net negative charge.

The dissociation of hydroxyl groups (OH^{-1}) on the surface of clays results at positions involving silicon atoms on broken edges of oxygen sheets (neutral and alkaline solution) from the reaction

$$Si - OH + H_2O \rightarrow Si - O^{-1} + H_3O^{+1} \qquad (63)$$

Additional formation of negative surface on clays may occur by adsorption of anions at cationic sites on broken edges of clay particles.

Because clays possess a high degree of negative character in neutral (pH 7) solution, certain predictions can be made:

(1) when anions (Cl^{-1}, SO_4^{-2}, SO_3^{-1}, and PO_4^{-3}) are in solution and adsorbed on clay surfaces, the clay-water-solute system would tend to remain dispersed. The degree of dispersion should be influenced more by multivalent than for monovalent species.

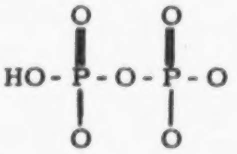
(2) the adsorption of cations on a negatively charged surface lowers the negative character (more positive) and the contact of this particle with a particle displaying greater negative character would effect flocculation. Multivalent cations would be more influencial than monovalent types because of their tendency to be more strongly adsorbed; therefore flocculation potential would probably vary, other things being similar, as $Al^{+3} > Mg^{+2} > Na^{+1}$ Flocculation would tend to increase with increase in concentration of cations.

(3) the amount of ionic hydration also influences dispersion and flocculation. Small ions like sodium become highly hydrated in solution such that their electrostatic charge becomes lowered because it is shielded by water. Thus small ions with a high degree of hydration and carrying a single positive charge become less effective in flocculating particles that do large ions with a lower degree of hydration and carrying a charge greater than one. Though this effect pertains mostly to cations and flocculation, it can be equally applied to effects of dispersion as controlled by anions in solution.

(4) the rate at which an ion moves in solution (ionic diffusion) may also influence flocculation-dispersion phenomena. Small ions, like Na^{+1} unless significantly hydrated, would tend to be more mobile than an ion such as Ca^{+2}. Therefore, a rapidly moving ion may find it much more difficult to get near the clay surface and be adsorbed than less mobile ions. Thus, cations with small diffusion coefficients in solution, would tend to be more influencial in flocculation of clay particles.

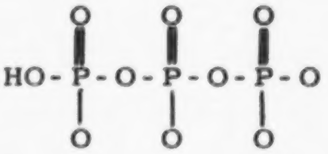
If surfactants are in solution with suspended solids, flocculation may occur if anionic and cationic surfactants are adsorbed on positively or negatively charged solids, respectively. Kenkiro and Tamotsu (1955) found that ferric oxide (positively charged) could be flocculated by as little as 10^{-2} moles/liter of a sodium salt of actyl sulfate ester (anionic surfactant); at much higher concentrations of this surfactant, the flocculated solid becomes redispersed. For cationic surfactants (pyridinium dodecylbromate), ferric oxide becomes flocculated at about one mole per liter; nonionic surfactants (polyoxyethylene glycol) were found to be without effect on this flocculation. In another study (Kenjiro, 1955) the influence of a cationic surfactant (pyridinium dodecylbromate) on the stability of a negatively charge sol (arsenic sulfide) was studied. This sol became flocculated by the cationic surfactant at concentrations as low as 5×10^{-4} moles per liter. These studies demonstrate the fact that oppositely charged particles and solutes, including surfactants like ABS, tend to flocculate at low surfactant concentrations and become redispersed at high surfactant concentrations.

Phosphates in detergent formulations also influence dispersive characteristics of suspended solids. The two types of phosphates used most commonly are the pyrophosphates (dimer chain)



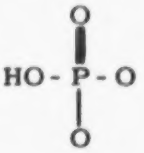
$$\mathrm{HO-\overset{O}{\underset{O}{P}}-O-\overset{O}{\underset{O}{P}}-O} \qquad (64)$$

with average anionic charge at pH 7 of 2.5, and tripolyphosphates (trimer chain)



$$\mathrm{HO-\overset{O}{\underset{O}{P}}-O-\overset{O}{\underset{O}{P}}-O-\overset{O}{\underset{O}{P}}-O} \qquad (65)$$

with average anionic charge at pH 7 of 3.5. In natural water these longer chain phosphates are believed to be degraded (depolymerized) into the monomer (orthosphosphate)



$$\mathrm{HO-\overset{O}{\underset{O}{P}}-O} \qquad (66)$$

with an average anionic charge of 1.5. The ability of phosphates to disperse kaolin suspensions has been studied (Van Wazer and Besmertuk, 1950). These authors concluded that the dispersive power of phosphates on these suspensions suggest that:

(1) the effect of increasing charge on anions is very important in the range monomer to dimer but insignificant beyond this range and

(2) dispersive effects may be attributed to the combined roles of anionic charge and the ability of phosphates to form complexes with the surface ions (cations) in the crystal lattice of kaolin.

If the polyphosphates depolymerize in surface water to orthosphosphate, then this form of phosphate may be significant to disperse solids (lower viscosity) in this environment.

Viscosity studies with ABS in solution

Because data on the viscosity of surfactant solutions with and without other substances in solution were not previously available, a study was made to determine the effect of surfactants on the viscosity of water containing bacteria and clay in suspension (Wayman and others, 1963e).

The viscosity of all solutions was measured with the aid of Cannon-Ubbelohde Semi-Micro Dilution Calibrated viscometers (figure 23). These viscometers may be employed to

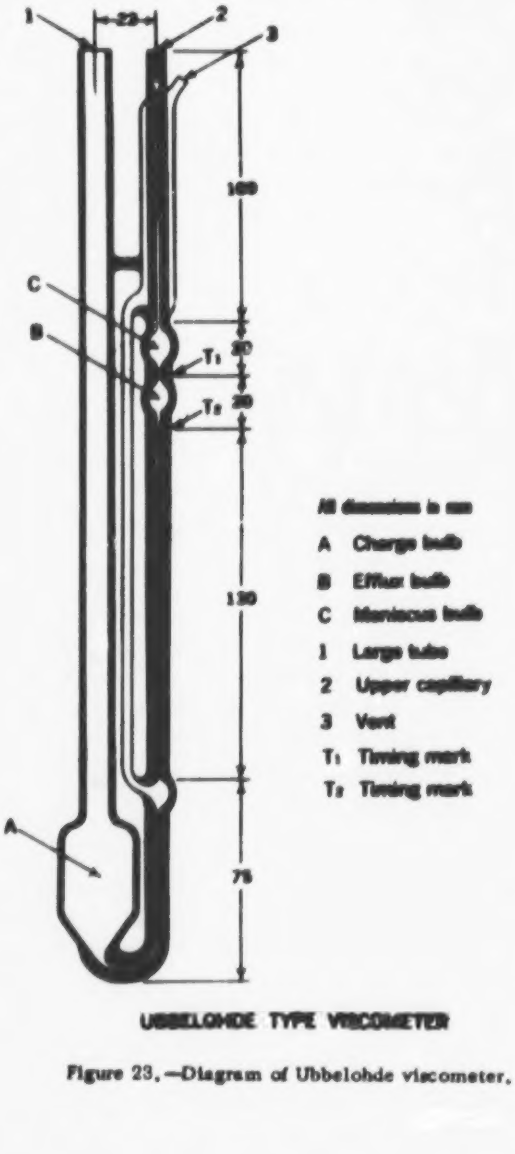


Figure 23.—Diagram of Ubbelohde viscometer.

measure viscosity in the range 0.2 to 20,000 centistrokes. The validity, assumptions, and use of such viscometers in measurement of viscosity have been reported previously (Cannon and others, 1960). In our study viscometers were employed to cover the range 0.8 to 28 centistrokes.

The influence of temperature on the viscosity of solutions containing 1000 of anionic, cationic, or nonionic solutions is shown in figure 24. For the range of temperatures to be encountered in water, all surfactants tested seem to flow at about the same rate as water. Therefore, surfactants in solution below

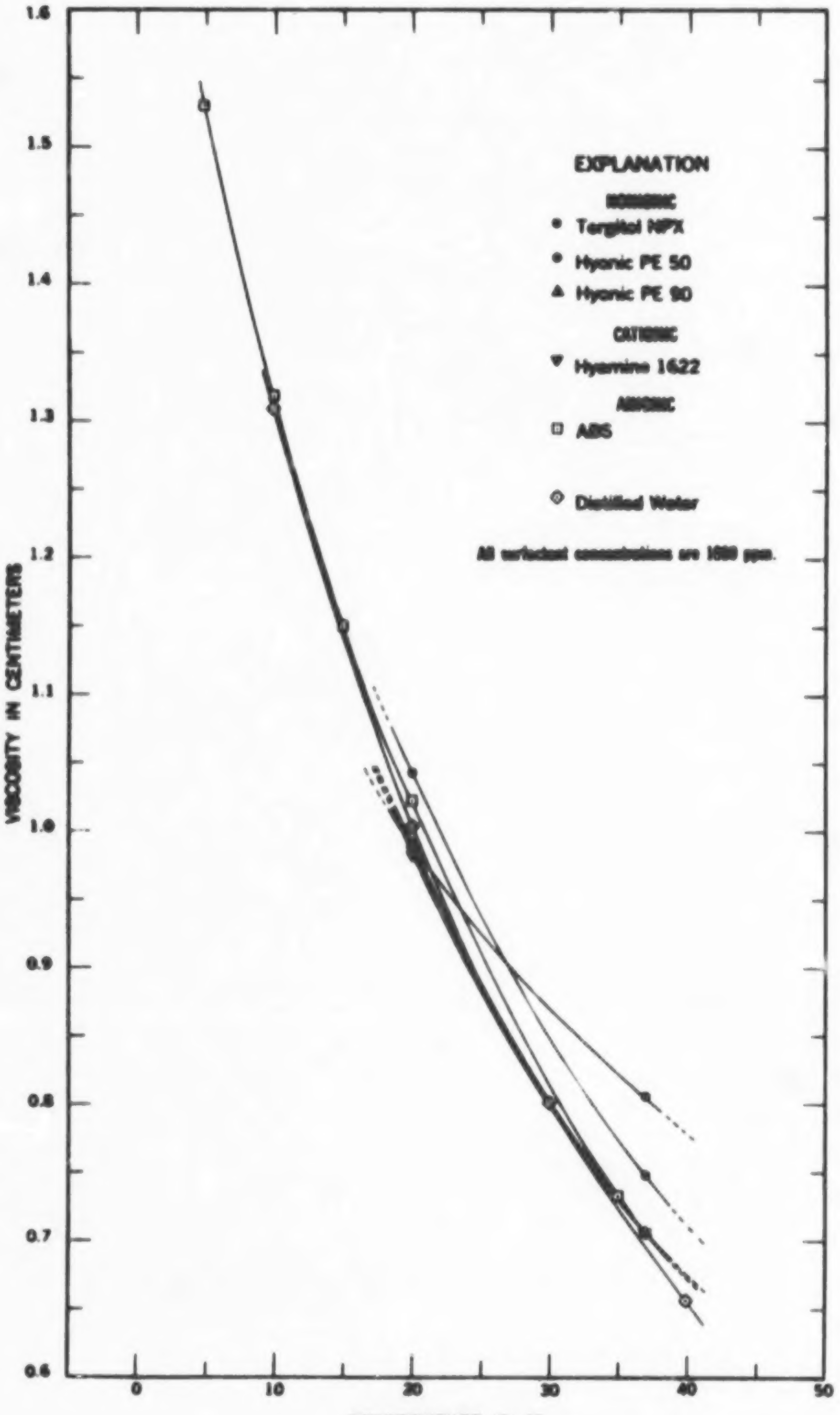


Figure 24.—Variation of viscosity with temperature for solutions containing 1000 ppm of various surfactants.

1000 ppm would not probably influence the viscosity of water.

The viscosity of solutions containing 500 ppm of various commercial detergents at 20°C and pH 6.8 is shown in figure 25. Most detergents show viscosities slightly above not significantly different from water at this temperature. Thus, neither surfactants nor builders in detergents seem to influence the viscosity of water without suspended solids.

Figure 26 shows the effect of bacterial concentration (*E. coli*) on viscosity of solutions containing surfactants (10 ppm) or detergents (10 ppm). Solutions containing as much as 100 million bacteria per ml have viscosities similar to that of water at this temperature. Thus, bacteria at these concentration levels cause no viscous effects.

To determine the effect of suspended and dissolved solids on viscosity, three series of clay suspensions were prepared using only the< 2-micron size fraction of three API (American Petroleum Institute) clays: montmorillonite (No. 26), illite (No. 35), and kaolinite (No. 2). The concentration of clay for the illite and kaolinite series ranged from 0.0 to 4.0 g (grams) per 100 ml of deionized water (pH 7) and for the montmorillonite series from 0.0 to 3.4 g per 100 ml of deionized water. The viscosity of each suspension was measured at 20°C. Each series

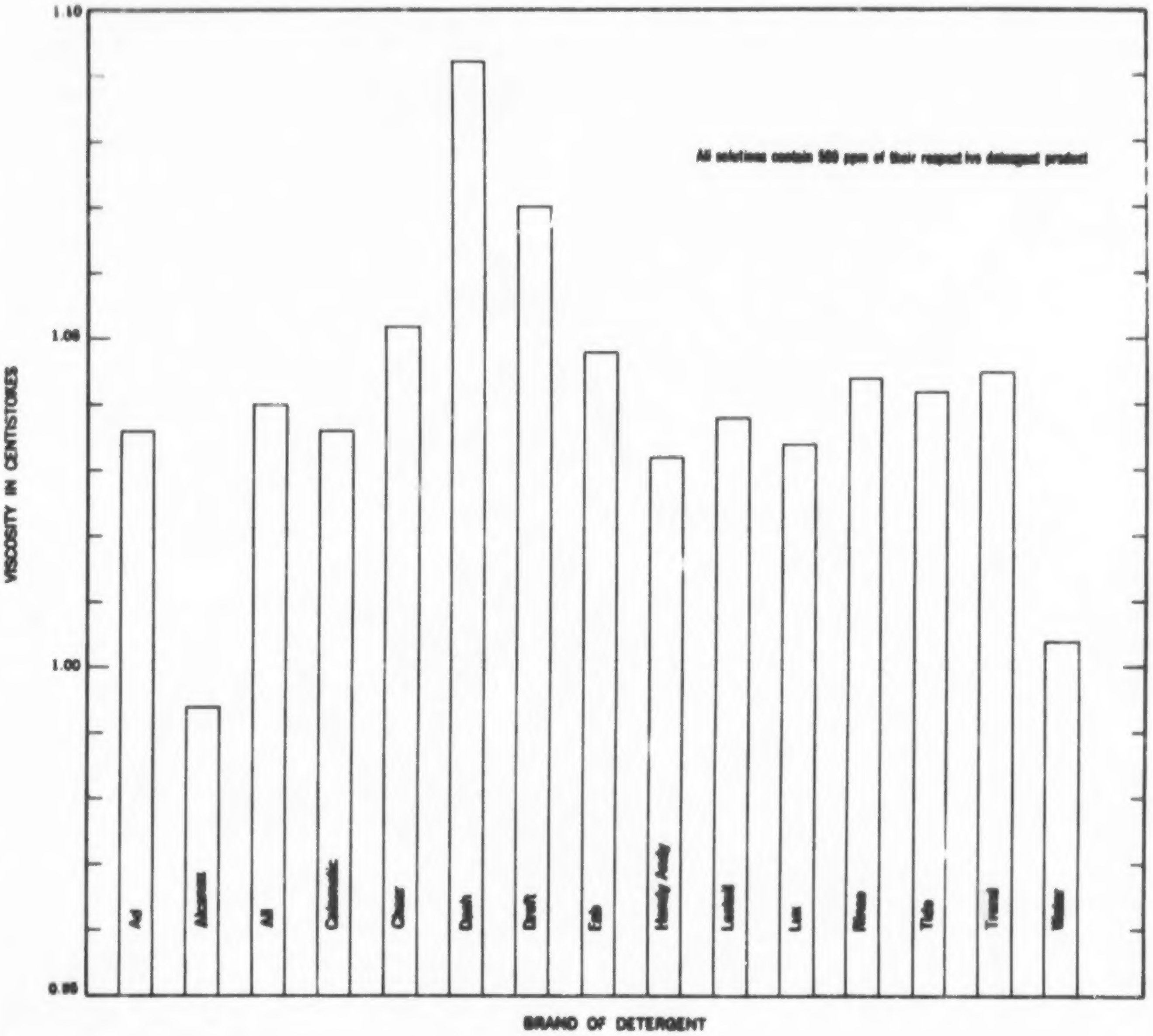


Figure 25.—Viscosity of solutions containing 500 ppm of various commercial detergents at 20°C and pH 6.8.

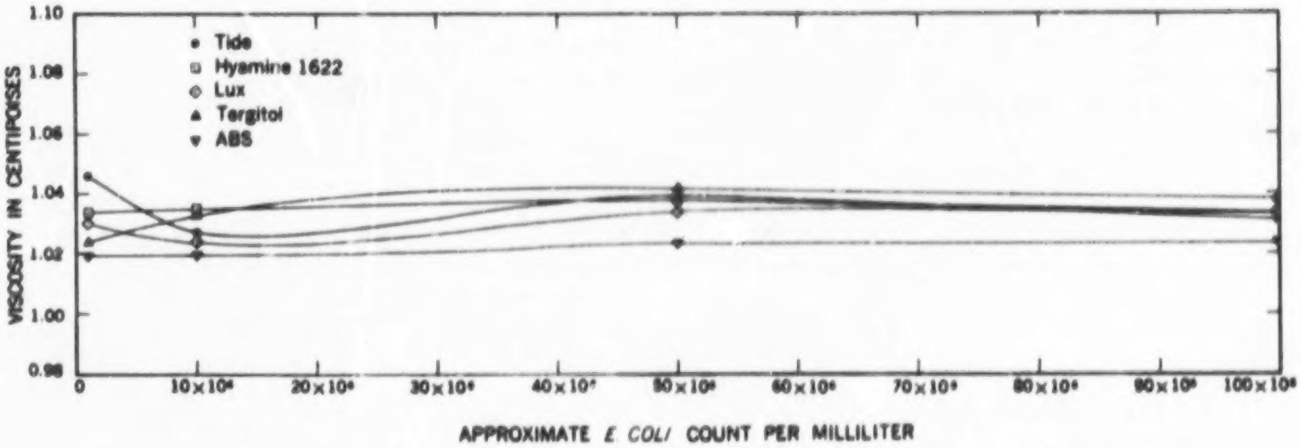


Figure 26.—Effect of bacterial concentration on viscosity of solutions containing 10 parts per million surfactants or detergents.

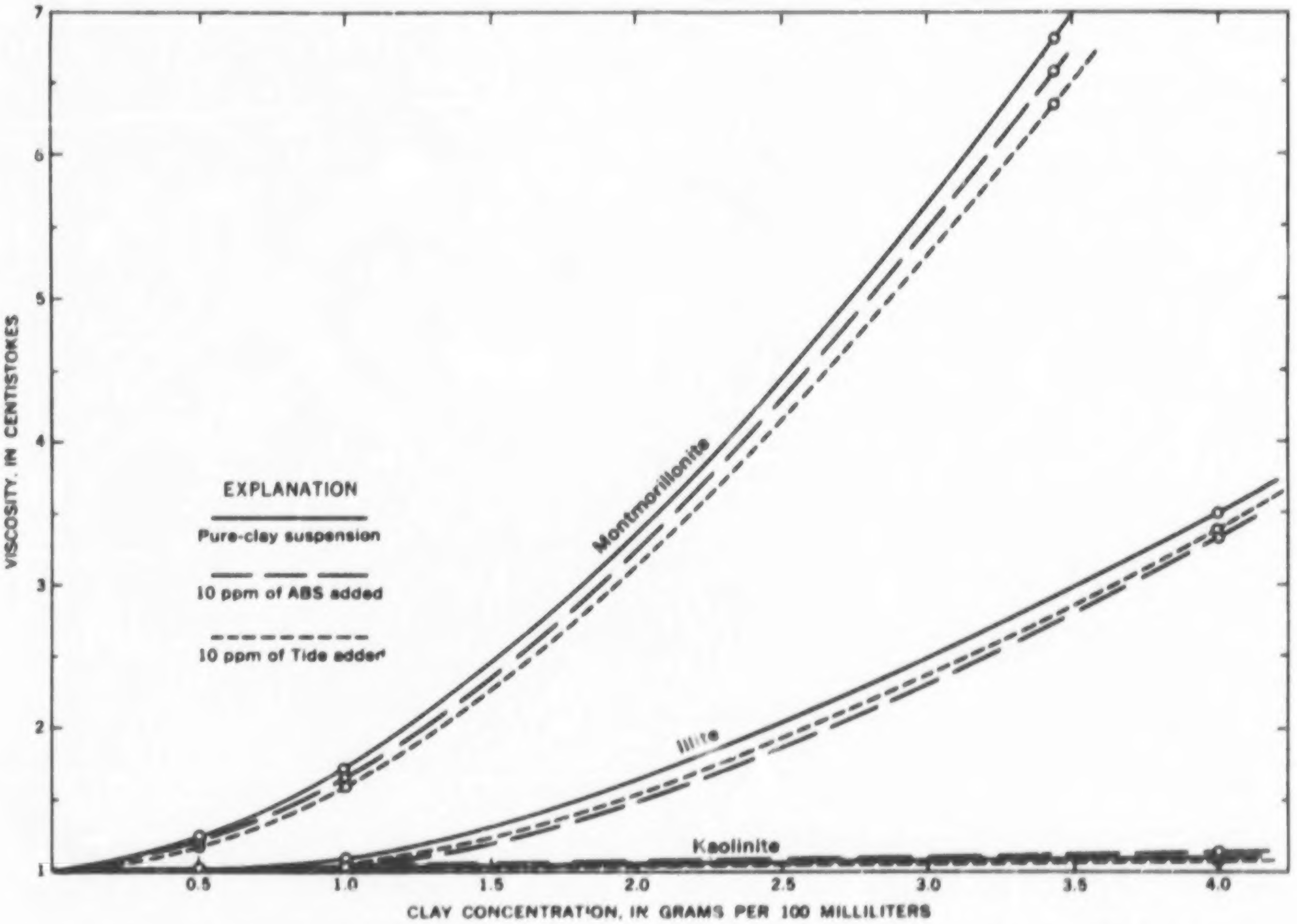


Figure 27.—Relation of viscosity to clay concentration and commercial-detergent components at 20°C and pH 7.

was repeated, but either 10 ppm of the anionic surfactant (ABS), or 10 ppm of commercial detergent (Tide) was added to each clay suspension. This commercial detergent consists of about 40 percent ABS and 60 percent unknown detergent builders.

Figure 27 shows the relation between viscosity and concentration of clay and detergent components for the 3 API clays at pH 7 and 20°C. Nither as much as 4.0 g of kaolinite per 100 ml of deionized water nor 10 ppm of ABS or other components in commercial detergent preparations significantly affects the viscosity of kaolinite suspensions. The viscosity of illite and montmorillonite suspensions begins to increase at concentrations of 1.3 and 0.1 g of clay per 100 ml of deionized water, respectively; components in commercial detergents tend to cause a slight decrease in the viscosity of these suspensions. Similar families of curves have been obtained for montmorillonite, attapulgite, and kaolinite suspensions in solutions of Calgon, sodium chloride, and hydrochloric acid (Searle and Grimshaw, 1959). This lowering of viscosity (dispersion effect) might be attributed to the repulsion of clay particles from adsorption of anions (ABS, chlorides, sulfates) from solution to effect a more dispersed system. The clay particles, already possessing a negatively charged surface at pH 7, become more negative if anions are adsorbed at cationic sites on such surfaces.

Changes in pH and temperature have marked effects upon the viscosity of clay suspensions. These effects were studied on pure clay suspensions consisting of 1.5 g of clay per 100 ml of deionized water. The pure clay suspensions were compared to clay suspensions containing 100 ppm of ABS or 200 ppm of Tide. The pH of the suspensions was adjusted by adding hydrochloric acid or sodium hydroxide; the observed changes in viscosity with changes in pH and temperature are shown in figures 28 to 30.

Figure 28 shows the effect of pH changes and of addition of surfactant (ABS) and detergents on the viscosity of kaolinite suspensions. At 10°C, a maximum viscosity for a pure kaolinite suspension occurs at a pH of about 4. Between pH 4 and 7, ABS and other components in detergent formulations cause a marked decrease in the viscosity. The results would seem to be most readily explainable on the basis of adsorption of ABS and other anions on clay surfaces to effect repulsion of particles in attainment of a more dispersed (less viscous) system.

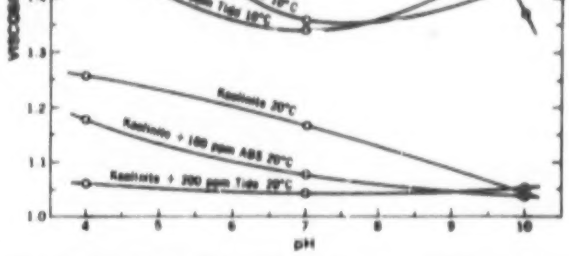


Figure 28. —Relation of viscosity of kaolinite suspensions to pH and commercial detergent components at 10°C and 20°C.

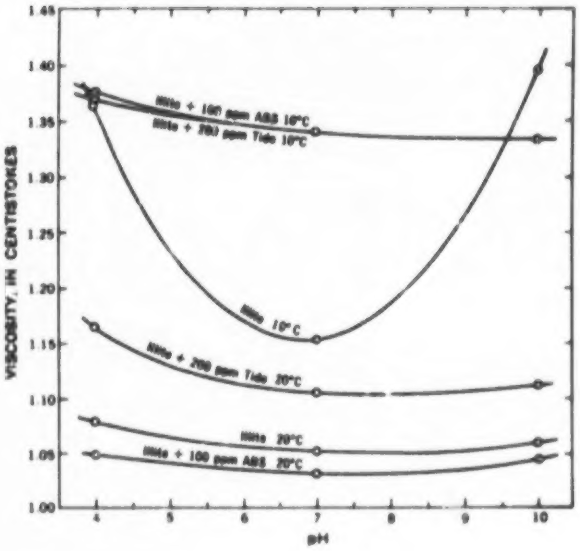


Figure 29. —Relation of viscosity of illite suspensions to pH and commercial detergent components at 10°C and 20°C.

Figure 29 shows the effect of similar treatment of illite suspensions. At 10°C, maximum viscosity of the illite suspension is at pH 4 and pH 10; a minimum viscosity is at pH 7. Addition of detergent ions tends to flocculate (to increase the viscosity) of this clay suspension through a wide range of pH but not drastically. At 20°C, viscosity for similar tests is less than at 10°C, and the viscosity varies less as the pH changes than at 10°C.

Figure 30 shows the effect of similar treatment of montmorillonite suspensions. At 20°C, a minimum viscosity occurs at pH 7; detergent components markedly reduce the viscosity between pH 4 and pH 7. At 10°C, the reverse occurs; that is, the detergent components increase the viscosity or flocculate the suspension. Earlier studies on purified montmorillonite (Street, 1958) indicated the general trend observed at 10°C but not at 20°C.

The results of the viscosity tests on montmorillonite suspensions are difficult to understand. However, previous investigators have

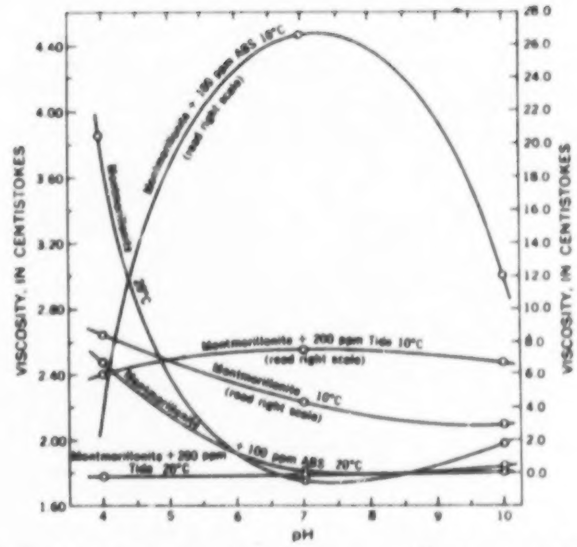


Figure 30.—Relation of viscosity of montmorillonite suspensions to pH and commercial detergent components at 10°C and 20°C.

indicated that the viscosity of clay suspensions can be explained in terms of electrokinetic phenomena with use of the Gouy-Freundlich diffuse double-layer concept and van der Waals attractive forces at the clay particle-solution interface. The concentration of the clay suspension (Coughanour and Norton, 1949), surface area of the clay (Johnson and Lawrence, 1942), and electrolytes in solution (Hauser and Hirshon, 1939; Speil, 1940; Johnson and Norton, 1941; and Kingery, 1951) influence electrical properties at the clay particle-solution interface and produce changes in the viscosity of clay suspensions. The role played by surface tension along, neglecting ionic effects, is of dubious importance in the viscosity of clay suspensions. Schwartz (1952) and Kingery and Francl (1954) suggest that wetting agents (surfactants and detergents) decrease the viscosity of clay suspensions. However, a detailed study of wetting agents in clay suspensions (Ormsby, 1960) indicated that surface tension seems to have only a minor effect upon the viscosity of clay suspensions. Several variables, some of which could not be considered in this study, influence the viscosity of clay suspensions. Because drastic changes in the viscosity of montmorillonite suspensions were determined in comparison to illite or kaolinite it seems reasonable to emphasize that more of the above variables influenced the flocculation properties (high viscosity) of montmorillonite suspensions than those of the other two clays.

Commercial-detergents components in kaolinte or illite clay suspensions slightly decrease and slightly increase the respective viscosities of these two clay suspensions as compared to the viscosity of water at the same temperature. At 10°C and pH 7, commercial-detergent components in montmorillonite suspensions can increase the viscosity to as much as 25 times that of water. This study has shown that the viscosity of clay suspensions depends on the composition of the clay, pH, temperature, and electrolytes (builders) in detergent formulations.

Because sewage and household waste water containing detergents and bacteria, but no suspended solids, have a viscosity similar to that of pure water, these solutions probably travel at the same rate as water for a given temperature. However, waste water containing clay in suspension, especially montomorillonite, can be as much as 25 times less mobile than similar water containing no suspended solids, for the conditions mentioned in this article. Thus, the flow of clay-water suspensions can be greatly altered by the presence of detergent components which may have significant influence in many areas of fluid-flow studies such as open-channel flow and sedimentation, flow in pipes, underground flow through fractures and solution openings, and in drilling-mud technology.

BIODEGRADATION OF SURFACTANTS IN DETERGENTS

The stability and presence of surfactants in soil-water environments presents multifaceted problems. Some of these problems can be related to cause and effect phenomena.

One aspect of cause and effect involves the relation between surfactant concentration and surface activity at the bacterial membrane-solution interface. If surfactants become too concentrated at this interface, the bacterial may become lysed or lysis may be initiated. Lysis is the complete biochemical destruction of the bacterial cell. Thus, surfactants in solution at certain critical concentrations may kill bacteria and prevent the possibility of biodegration of surfactants. In effect, surfactants react with the bacterial cell membrane and kill the organisms by releasing intracellular components and initiating the "autolytic" breakdown of cellular nucleic acids, proteins, and structural elements. The intensity of lysis depends on the specific type of organism and the environmental conditions. In general, cationic surfactants possess a higher degree of lytic effect than anionic surfactants; this effect can be attributed to the greater attraction of the positively charged cationic surfactant than the negatively charged anionic surfactant to the bacterial surface which is negatively charged. In a previous study the amount of cationic or anionic surfactant required to produce a lysis (killing) of 99.9 percent of micrococcus lysodeikticus suspensions was studied (Gilby and Few, 1957); for the cationic surfactants (dodecylamine hydrochloride and dodecyltrimethylammonium bromide) respective concentrations to produce this effect were 2.1 x 10-4 molar and 4.0 x 10-4 molar as compared to the respective anionic surfactant (sodium dodecyl sulfate and sodium dodecyl sulfonate) concentrations of 12.0 x 10-4 molar and 25.0 x 10-4 molar. Thus, the effectiveness of surfactant reactivity with bacterial cell membrane for the specific ions $NH_3{}^{+1}$:$N(CH_3)_3{}^{+1}$:$SO_4{}^{-1}$:$SO_3{}^{-1}$ is 1:2:6:13. Similarly, the preferential adsorption of cations over anions on bacterial cell walls was investigated (Salton, 1957); the amount of cetyltrimethylammonium bromide (cationic surfactant) adsorbed (μg per mg-dry weight) on staphylococcus aureus, strep. faecalis, and escherichia coli was 150, 350, and 385, respectively. For comparison, the value for adsorption of the anionic surfactant Aerosal OT (dioctyl sodium sulphosuccinate) on straphylococcus aureus was 30.

Becaus bacteria in soil, water, or sewage may be lysed by surfactants and prevent biodegradation, a study was made of the factors influencing the survival of Escherichia coli in surfactant solutions (Wayman and others, 1963-d). A previous study McKinney (1956) employed pure bacterial cultures in metabolic studies with ABS as the sole source of carbon; it was concluded that:

(1) 34 ABS metabolizing type of soil bacteria species (16 Alcaligenes, 13 Pseudomoncis, 3 Aerobacter, 1 Escherichia, and 1 Flavobacterium) could grow in solutions containing 35 ppm of ABS.

(2) Mixtures of these bacteria were able to metaboliz as much as 1000 ppm of ABS but metabolism is retarded at the higher concentration; and that ABS is incompletely metabolized in sewage activated sludge systems. Manganelli (1952) found that 100 ppm of the ABS (Nacconol N. R.) were not toxic to coliform bacteria in sewage oxidation studies. Later studies (Manganelli and Crosby, 1953) indicated that 100 ppm of Nacconol N. R. were toxic to micro-organisms in activated sludge sewage systems. Degens and others (1955) showed that 30 ppm of ABS adversely affected bacteria in activated sludge; this influence was observed at 12.5 ppm of ABS but was not recognized at 5.0 ppm. Thus, the toxic effect of ABS on sewage of soil bacteria is conflicting.

In this study the influence of temperature, pH, and certain components in commercial detergents on survival of Escherichia coli, one of the common bacteria normally present in human intestines and indicative of fecal contamination in water, was investigated. The literature lists but few previous studies on survival of these bacteria. Carlucci and Pramer (1960) indicate that Escherichia coli have optimum survival rates in acid water (pH 5), in saline water, and in water containing inorganic nutrients, $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$, and organic matter (glucose, peptone, sewage volatine solids, and cysteine). Dyadichev (1959) points out that the chemical quality of water, temperature, pH, organic nutrients, hydrologic conditions of a water basin, and other factors influence survival of Escherichia coli, but he provided no experimental documentation. In our study, changes in bacterial reactivity were measured indirectly by determining the length

Table 16.—*Concentrations, temperatures, and pH of bacterial solutions investigated*

Solution	pH 4			pH 7			pH 10		
	10°C	20°C	35°C	10°C	20°C	35°C	10°C	20°C	35°C
Distilled water	------	------	------	X	X	X	------	------	------
10 ppm ABS[1]	X	X	X	X	X	X	X	X	X
100 ppm ABS	------	------	------	X	X	X	------	------	------
1,000 ppm ABS	------	------	------	X	X	X	------	------	------
5 ppm ABS plus 10 ppm PO_4	X	X	X	X	X	X	X	X	X
10 ppm ABS plus 10 ppm PO_4	X	X	X	X	X	X	X	X	X
10 ppm ABS plus 10 ppm PO_4 plus 1 ppm CMC[2].	X	X	X	X	X	X	X	X	X
12.5 ppm commercial detergent	X	X	X	X	X	X	X	X	X

[1] ABS==alkylbenzenesulfonate.

[2] CMC==carboxymethylcellulose.

of time a specific number of bacteria survived at varying temperatures, pH, and concentration of detergent component.

Bacterial solutions were prepared by adding pure cultures of bacteria (Escherichia coli), sodium hydroxide or hydrochloric acid (for adjustment of pH), and detergent components to sterilized, distilled, and deionized water. Bacteria were added to different solutions at temperatures to cover the range usually found in ground water, and at selected pH to include the acid through basic range as shown in Table 16. The prepared solutions were placed in constant-temperature water both (±0.1°C) and were sampled periodically by sterile technique. One ml. of solution sampled in duplicate was removed from each of the preparations and mixed with McConkey's agar. The agar plates were incubated at 37°C ±1°C for 72 hours, and the number of bacteria remaining in the sampled solution was determined by the plate-count method (American Public Health Association and others, 1960). Two experimental difficulties that may have influenced these studies are (1) the inability to place identical starting amounts of bacteria in each test solution and (2) the possible variation in the age and virility of the different stocks of bacteria used. Either of these variables might influence the bacterial survival rate, but what that influence is, if any, is unknown to the authors.

Figure 31 shows the survival in solutions of varying pH and ABS concentration at 10°C. Bacteria apparently can survive for many days in distilled water at low temperature without any available nutrient; this effect might be attributed to survival of bacteria from utilization of their own products of metabolism. In solutions containing 10 ppm of ABS, bacteria survive longer at a pH of 7 than at either pH 4 or 10. In alkaline media (pH 10) bacteria initially seem to experience a certain degree of shock and many die off rapidly; however, the surviving bacteria can apparently adjust to this environment and recover and multiply for a short period of time. Neutral solutions (pH 7) containing as much as 100 ppm of ABS are not toxic to bacteria, whereas solutions containing 1,000 ppm are toxic. The rapid death rate at the higher concentration of ABS may be attributed to the high degree of surface activity at the interface between the bacterial membrane and the solution. Changes in permeability of the membrane caused by adsorption of ABS probably alter normal metabolic processes of bacteria to produce this effect. Hotchkiss (1945) has indicated that 500 ppm of dodecyl benzenesulfonate (Santoese) kills staphlococci bacteria.

Figure 32 shows survival time of bacteria in solutions of varying pH and ABS concentration at 20°C. In solutions containing 10 ppm of ABS, maximum survival was at pH 7 and pH 10. At pH 7, solutions containing either 100 or 1000 ppm of ABS were highly toxic to bacteria; however, the toxicity is less pronounced than that in solutions containing 100 ppm of ABS at a pH of 4.

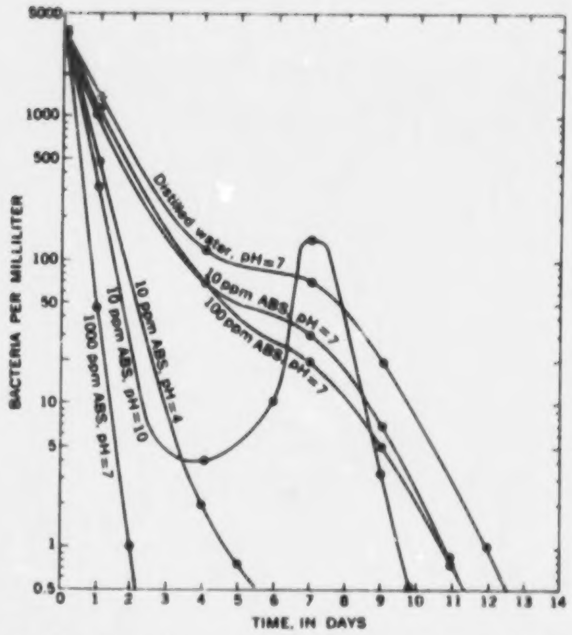


Figure 31.—Survival time of bacteria in solutions of varying pH and concentrations of ABS at 10°C.

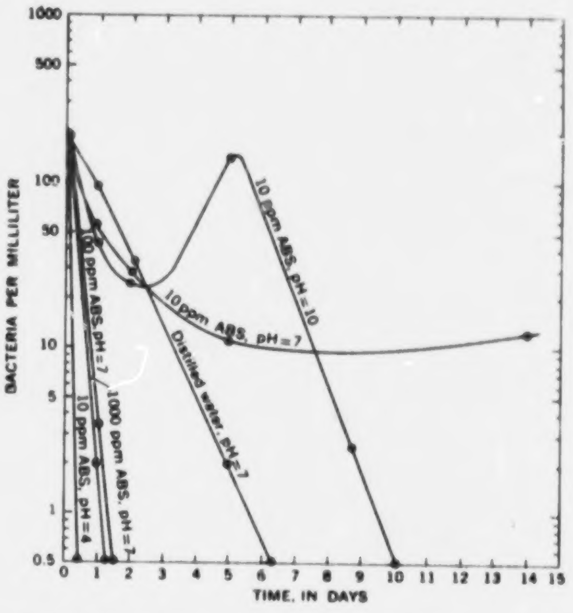


Figure 32.—Survival time of bacteria in solutions of varying pH and concentration of ABS, at 20°C.

Figure 33 shows the survival time of bacteria in solutions of varying pH and ABS concentration at 35°C. Bacteria do not persist at 35° regardless of pH or ABS concentration when this is the only source of carbon.

Figure 34 shows survival time of bacteria in solutions containing both ABS and phosphate at 10°C. At this temperature, phosphate acts as an inorganic nutrient for the bacteria through a pH range of 4 to 10, although a pH of 4 seems most detrimental to survival.

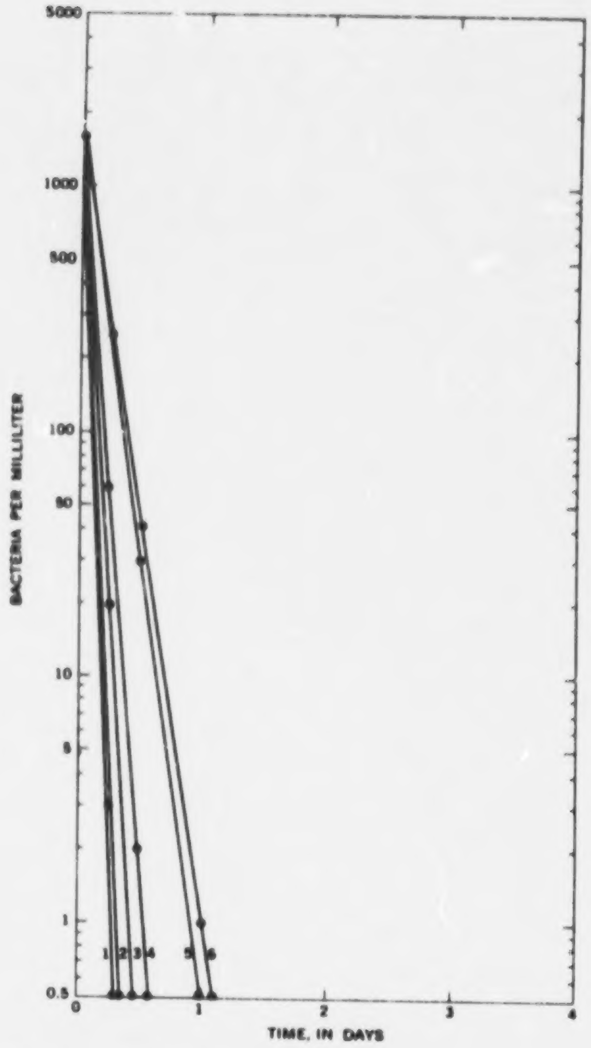


Figure 33.—Survival time of bacteria in solutions of varying pH and concentration of ABS at 35°C.

Similar experiments at 20°C and 35°C indicated a maximum survival of 4 days for bacteria at a pH of 7.

Figure 35 shows the survival of bacteria in solutions containing 10 ppm of phosphate, and 1 ppm of carboxymethylcellulose. Maximum survival times are in solutions of pH 7 and pH 10 at both 10°C and 20°C. The small amount of carboxymethylcellulose seems to be a very effective nutrient. Low pH and high temperature again seem most detrimental to survival. The bacterial revival indicated by the curve at 10°C and pH 10 probably would have receded within a few days if the test had been continued as shown in figures 31 and 32.

Figure 36 shows the survival time of bacteria in solutions containing 12.5 ppm of a commercial household detergent (approximately 40 percent ABS plus unknown builders). In

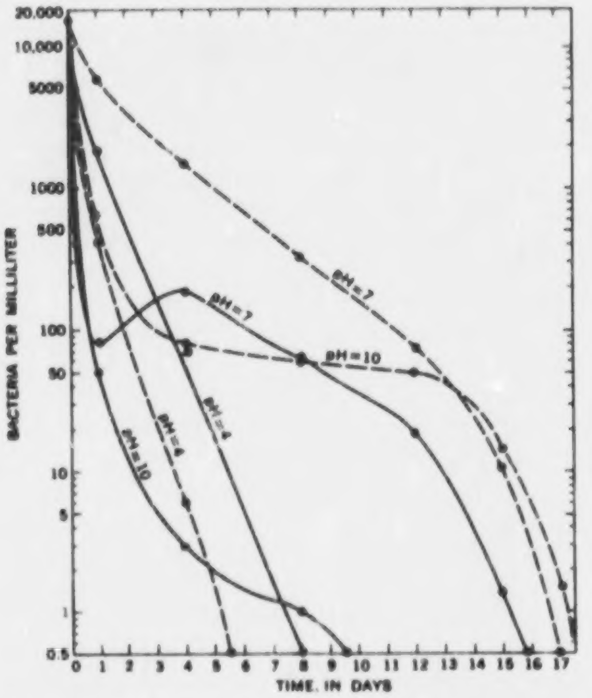


Figure 34. —Survival time of bacteria in solutions of varying pH and concentration of ABS and 10 ppm of phosphate at 10°C.

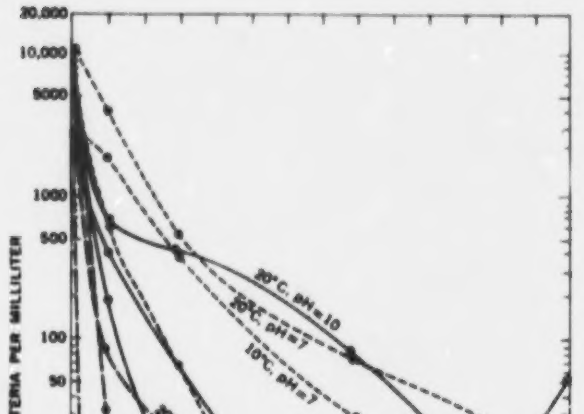


Figure 35. —Survival time of bacteria in solutions containing 10 ppm of ABS, 10 ppm of phosphate, and 1 ppm of carboxymethylcellulose, at varying pH and temperature.

general, the optimum conditions for bacterial survival were in solutions at a pH of 7, regardless of temperature, or in alkaline media (pH 10) at 20°C. At low pH and at 35°C and pH 10, the solutions were highly toxic to bacteria.

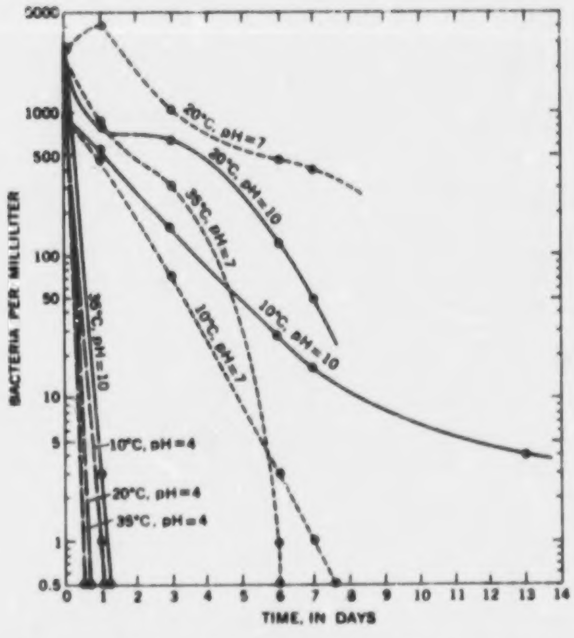


Figure 36. —Survival time of bacteria in solutions containing 12.5 ppm of household detergent, at varying pH and temperature.

The data obtained from this study suggest that a number of considerations are involved with respect to the ability of bacteria to degrade surfactants like ABS and contrariwise not to be poisoned by ABS; it is also significant to indicate that inability of soils to remove bacteria constitutes a potential pollution to ground water. In either case conditions contributing to survival of coliform bacteria (enteric) in detergent solutions are:

(1) Low temperature of water (less than 20°C).

(2) Neutral pH (about 7) and in some solutions alkaline pH (about 10).

(3) Phosphate, carboxymethylcellulose, and other constituents of commercial detergents.

In general bacteria seem to disappear logarithmically with respect to time. Low concentrations of ABS (10 ppm or less) do not prolong growth any more than distilled water and would be expected to be non-toxic in water. High concentrations of ABS (100 to 1000 ppm) are toxic to coliform bacteria; the toxicity, which kills the bacteria, probably is due to changes in permeability of the bacterial membrane which initiates or develops lysis.

Our study shows that the survival of coliform bacteria in water solutions depends upon

ABS concentration, pH, temperature, and inorganic and organic nutrients in detergents.

Biodegradation Studies

Unless bacteria can survive in water containing ABS, the degradation of this compound would not be achieved. Certain parameters influencing their survival were given in the previous section.

In addition to bacterial survival, oxygen must be available in water because of the biochemical oxidation involved in the degradation of ABS or surfactants. Another cause and effect relationship must also be considered regarding oxygen transfer from air into water when ABS is in solution. Treusdale and Downing (1954) have presented data on the solubility of oxygen in distilled-deionized water as a function of temperature as shown in figure 37; data are also listed on oxygen solubility in water for chloride concentration of 5,000 ppm. Chloride in solution can lower the amount of oxygen solubility but not appreciably.

If surfactants like ABS are in solution, the exchange coefficient between air and water is notably reduced. An evaluation of oxygen transfer from air to water along an open chennel 360 feet long (Truesdale, 1961) indicated that the dissolved oxygen in clean water increased from about 1 ppm at the entrance to about 5 ppm at the other end; the same water containing 1 ppm of ABS adsorbed only 3.5 ppm of oxygen indicating the effect of ABS on oxygen transfer from air. The same investigator also studied the amount of oxygen transfer from rivers which contain sewage effluents. The oxygen transfer rate was notably reduced in studies containing sewage effluent plus 1 ppm of ABS as compared to those containing only the sewage effluent (no ABS present). The effects were less pronounced than those obtained with pure water.

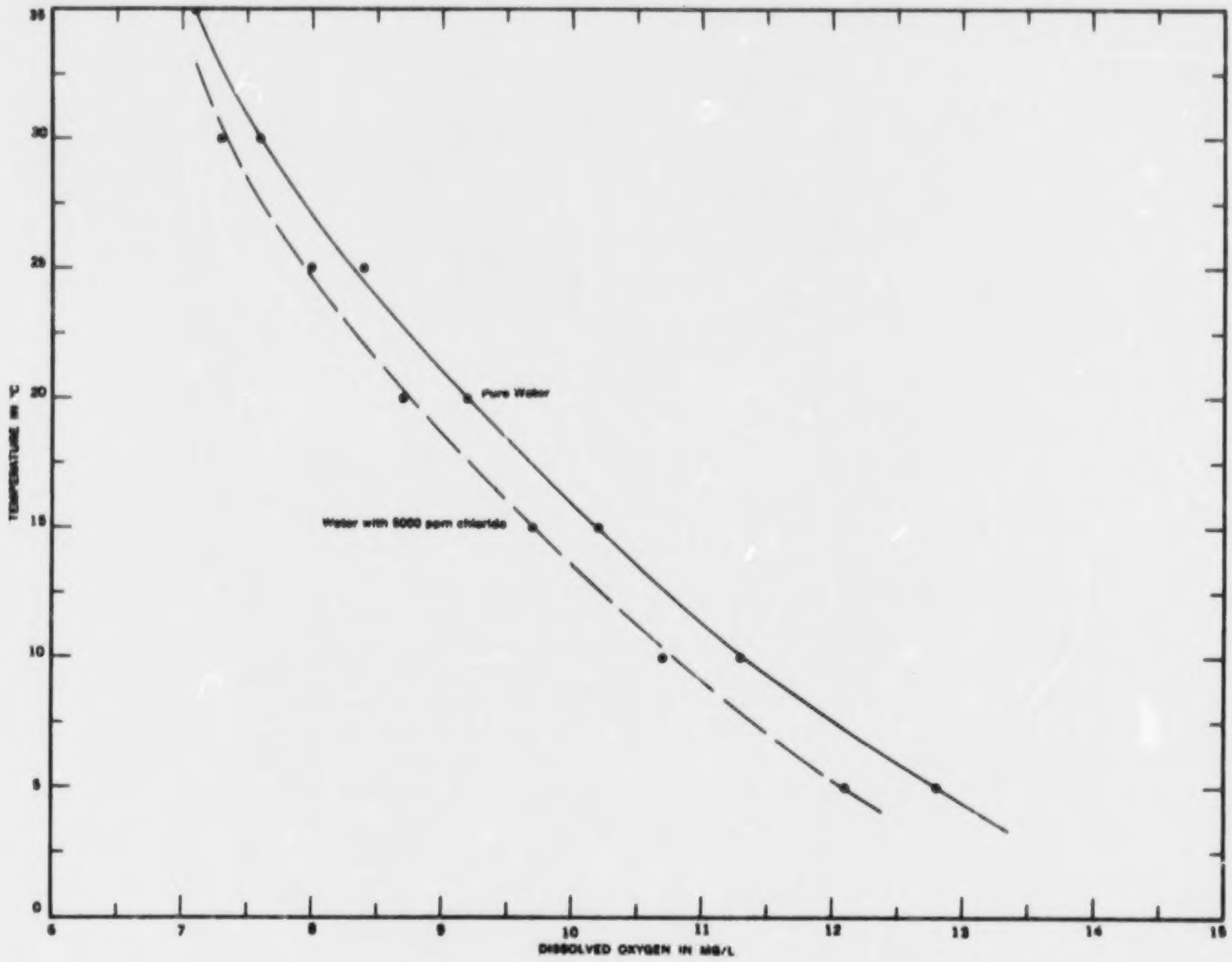


Figure 37. —Solubility of oxygen in water with and without dissolved solids.

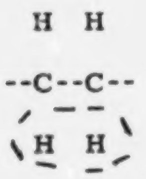
Thus, the amount of oxygen entering water with ABS in solution has two significant aspects regarding pollution:

(1) It may impede the biodegradation of ABS because of a paucity of available oxygen required by bacteria and

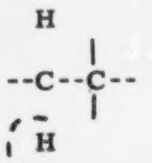
(2) It may have an adverse effect upon fish because of insufficient oxygen necessary for their survival.

Previous Studies

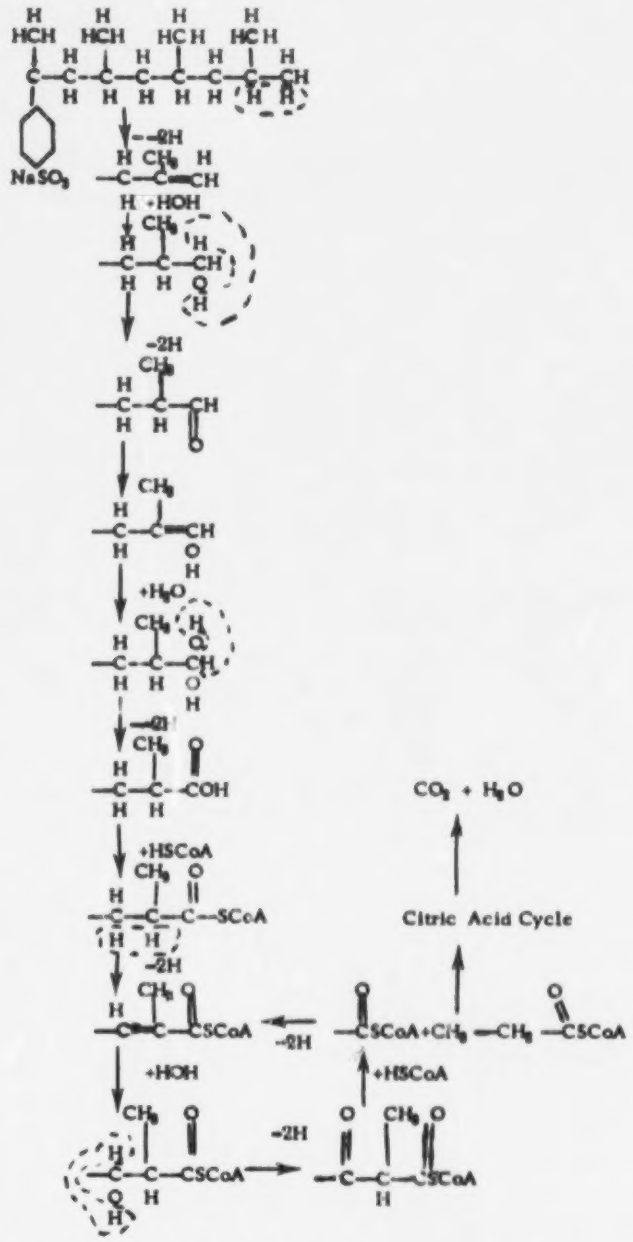
The inability of sewage, soil, and water bacteria to completely degrade ABS in commercial detergents has been known for sometime. Creditable contributions to our knowledge in this field have been those of Hammerton (1955), and Burnop and Bunker (1960). The reason for incomplete degradation is usually attributed to structure of the ABS; the highly branched types of ABS as shown in (20), (21), and (22) are representative of these structures. McKinney and Symons (1959) and Swayer and Ryckman (1957) believe the branched hydrocarbon side chain of ABS is metabolized by beta oxidation until if reaches the quaternary carbon. The ABS metabolism starts with the terminal methyl group (CH_3) on the hydrocarbon side chain. The terminal group is oxidized by enzymes to a carboxyl group. Then the hydrocarbon side chain is metabolized until it reaches the quaternary carbon. The normal removal of hydrogen occurs in pairs as shown below



but with the quaternary block the following probably occurs (McKinney and Symons (1959):

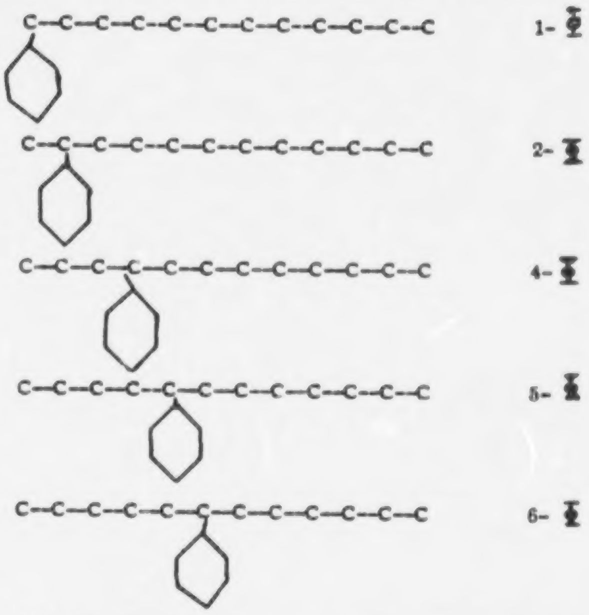


The quaternary carbon is believed to be located at the point where the hydrocarbon side chain joins the benzene ring. The complete theoretical beta oxidation of ABS is shown below (McKinney, 1956):



Because of the resistance of branched-chain ("hard") types of ABS to rapid degradation, detergent companies have been working vigorously in terms of outlay of money and research effort on newer types of ABS that degrade more completely and much more rapidly. Structures (23) and (24) represent types of these newer types of ABS. With regard to the newer, straight-chain ("soft") ABS, certain conclusions may be reported in essentially aerated water systems (Swisher, 1963; Burnop, 1960; and Chemical and Eng. News, June 3, 1963):

(1) Degradation occurs most rapidly, other things being equal, the nearer the sulfonate is located to the end of the hydrocarbon chain. Swisher (1963) emphasizes this point for a number of phenyl (Φ) dodecane sulfonates as shown in figure 38 with notation below:



(2) Between alkyl chain lengths C_6 and C_{12}, rate of ABS degradation increases with increase in chain length (Swisher, 1963). (Figure 39); with increased chain length between C_{12} to C_{14}, C_{13} degrades faster than C_{15} which degrades more rapidly than C_{14}. (Figure 40, Swisher, 1963). Swisher (1962a) has suggested from his studies that ABS may be degraded by alternate metabolic routes in addition to the commonly accepted beta oxidation. It is suggested that this oxidation may initially involve the breakdown of one of the terminal methyl groups to a carboxyl with subsequent oxidation along the path indicated for quaternary carboxylic acids (McKinney, 1961). It is also pointed out that the initial attack might occur at an intermediate point along the straight chain with subsequent rupture, the attack being facilitated by increased chain length.

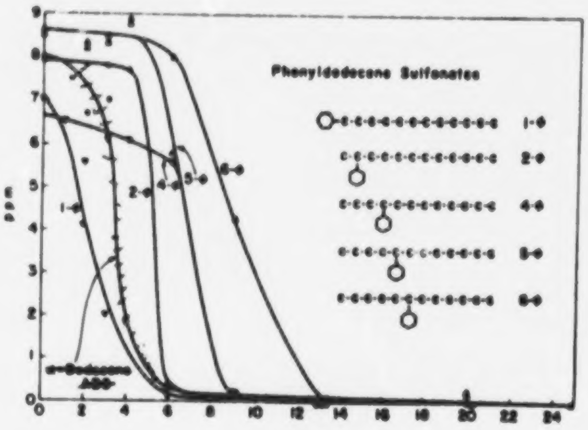


Figure 38. —Rate of biodegradation of straight chain phenyldodecane sulfonate with respect to location of benzene ring.

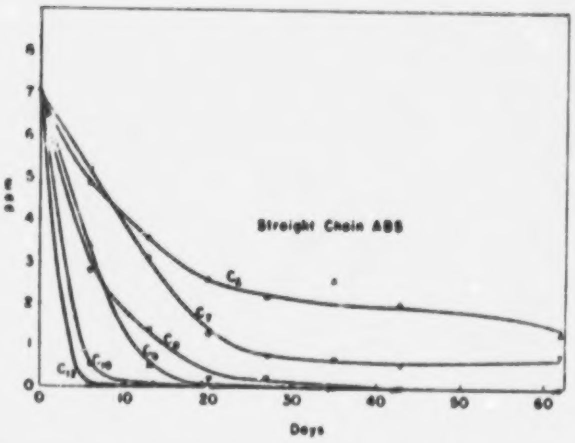


Figure 39. —Rate of biodegradation of straight-chain ABS with lengths of alkyl chain between C_6 to C_{12}.

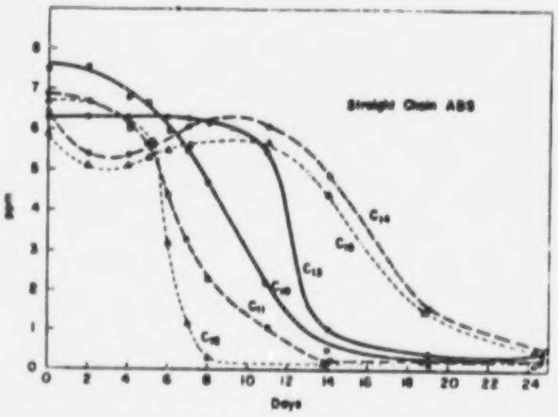


Figure 40. —Rate of biodegradation of straight-chain ABS containing C_{12} to C_{15}.

Other additional effects of structure of newer types of ABS are related to its toxic effects on fish which may be summarized as: (Chemical and Eng. News, June 3, 1963)

(1) toxicity increases with increase in chain length and

(2) toxicity of single isomers decreases from the C-2 position (2 Φ), passes through a minimum, then increases to the midchain position isomer, C-6 position (6 Φ) for a C-12 type ABS.

Aerobic and Anaerobic Studies

Because the above studies pertain essentially to aerated water, an investigation was made for both aerobic and anaerobic conditions in the temperature range 10° C to 35°C on biodegradation of ABS surfactants. It was intended that the data should allude to questions such as:

(1) do newer types of straight-chain ABS break down equally well in both aerobic and anaerobic water environments

(2) has bacterial concentration any influence on degradation and

(3) does temperature influence this degradation. The results might be applied to ABS breakdown in aerobic or anaerobic ground water environments, to diluted sewage in rivers, and to seasonal temperature changes.

The sufactants employed in the study were a branched-chain ABS (99 percent pure), domestically produced straight-chain ABS, and a German straight-chain ABS. The source of bacterial utilized in this study was obtained from the South Platte River water sampled near the discharge pipe of the Denver Treatment Plant effluent. The composition of selected constituents of this water over a two-year period indicated the following ranges of concentration: total bacteria, 100,000 to 6,000,000 per ml; detergent (ABS), 2.0 to 8.0 ppm; dissolved solids, 450 to 1,000 ppm; dissolved oxygen, 0.0 to 5.0 ppm; biological oxygen demand, 125 to 250 ppm; and pH, 6.2 to 8.1.

Solutions were prepared by dilution of the river water 10 to 100 times with distilled water or by using the river water undiluted to give starting concentrations of total bacteria or coliform, and other enteric bacteria that ranged from 2,000 to 5,000,000 per ml. As much as 13 ppm of any one of the types of ABS were added to the starting solution. All solutions were prepared in one liter volumetric containers and reduced to 500 ml for testing purposes. Sample solutions were placed in a constant temperature both accurate to ±0.1° C. To assess the amount of ABS breakdown by bacteria, samples were periodically removed and analyzed for ABS, total bacteria or coliform and other enteric bacteria or both. ABS was determined by the methylene-blue method. Total bacteria and coliform (including enteric) bacteria were determined by the pour-plate technique using Nutrient and MacConkey agars, respectively, at an incubation temperature of 37° C for 72 hours. The anaerobic systems contained only the amount of residual dissolved oxygen in solution, which ranged from 25 to 50 percent of the saturation value before dilution with deaerated water. The aerobic systems contained a continuous source of oxygen that was supplied from filtered laboratory air at constant flow rate and approximating saturation values.

Figure 41 shows the degradation of both branched-chain ABS and straight-chain ABS (domestic) under anaerobic conditions at 10°C for starting concentrations of 2,000 coliform and other enteric bacteria per ml and 6,000 total bacteria per ml. It is apparent that neither type of ABS can be significantly degraded under these conditions even up to 50 days. About 8 to 10 days are required for the bacteria to become acclimatized to their environment before any amount of sustained growth. The bacterial growth curves indicate that the types of bacteria indicated thrive well in this anaerobic environment but without any significant ABS breakdown. The survival of bacteria in these solutions must be explained on the basis of other nutrients in solution or perhaps metabolic products from bacterial activity. It is also significant to indicate that sewage effluent or river water bacteria may survive for long periods of time under anaerobic conditions; this suggests the existence of facultative anaerobes in these solutions but their ability to degrade ABS is poor.

Figure 42 shows the effects at 10° C (anaerobic conditions) with higher initial bacterial concentrations. The data show effects similar to those of Figure 33. Increased concentration of bacteria, at this level, seems to have no influence on degradation of ABS.

Figure 43 shows the effects of ABS degradation in undiluted river water (1,450,000 total bacteria per ml) at 10° C for both aerobic and anaerobic conditions. Branched-chain ABS cannot be significantly degraded under aerobic or anaerobic conditions. Significant amounts of straight-chain ABS can be degraded after about 6 to 8 days under aerobic conditions. At this temperature straight-chain ABS seems to degrade more rapidly and completely than branched-chain ABS but high initial starting concentrations of bacteria and an extensive amount of time (about one week) are required. The results also indicate that the anaerobic bacteria survive well in this undiluted water,

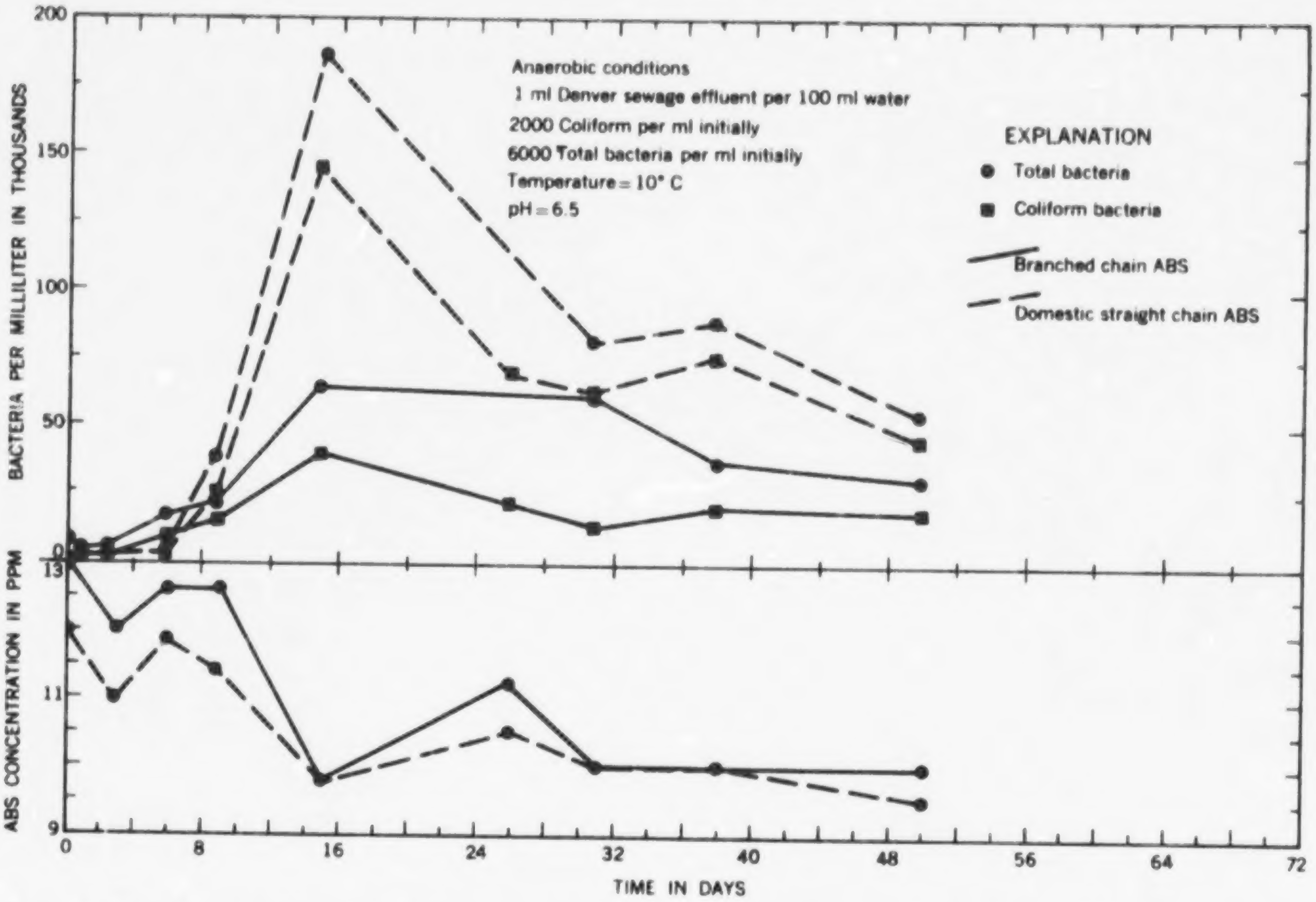


Figure 41. —Degradation of branched-chain and straight-chain ABS under anaerobic conditions at 10° C in river water dilute 100 to 1.

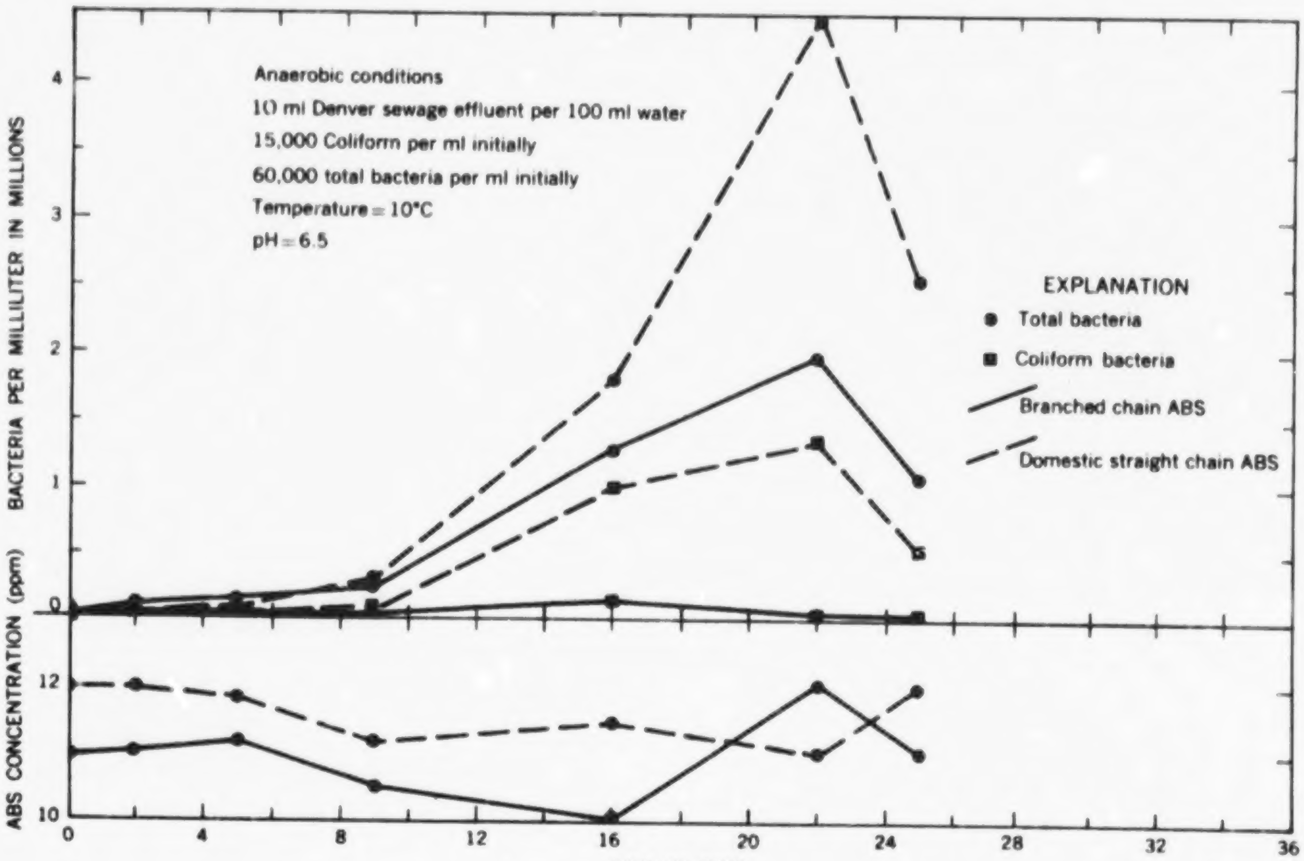


Figure 42. —Degradation of branched-chain and straight-chain ABS under anaerobic conditions at 10° C in river water diluted 10 to 1.

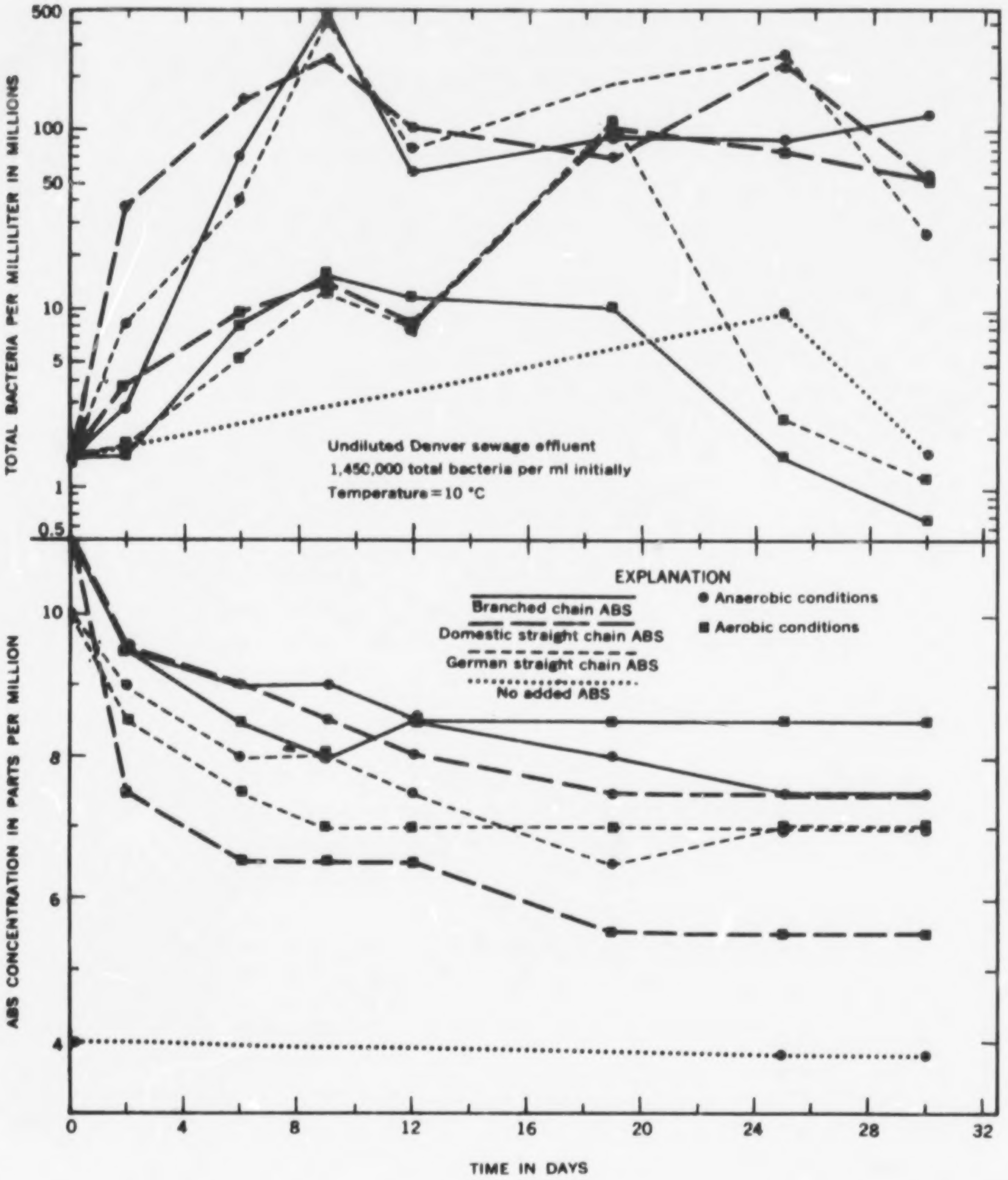


Figure 43. —Degradation of branched-chain and straight-chain ABS under aerobic and anaerobic conditions at 10°C in undiluted river water.

but most likely on nutrients in solution, other than ABS. The abundance of nutrients in solution seem to eliminate extensive amounts of time for bacteria to become acclimated to their environment as compared to the diluted systems.

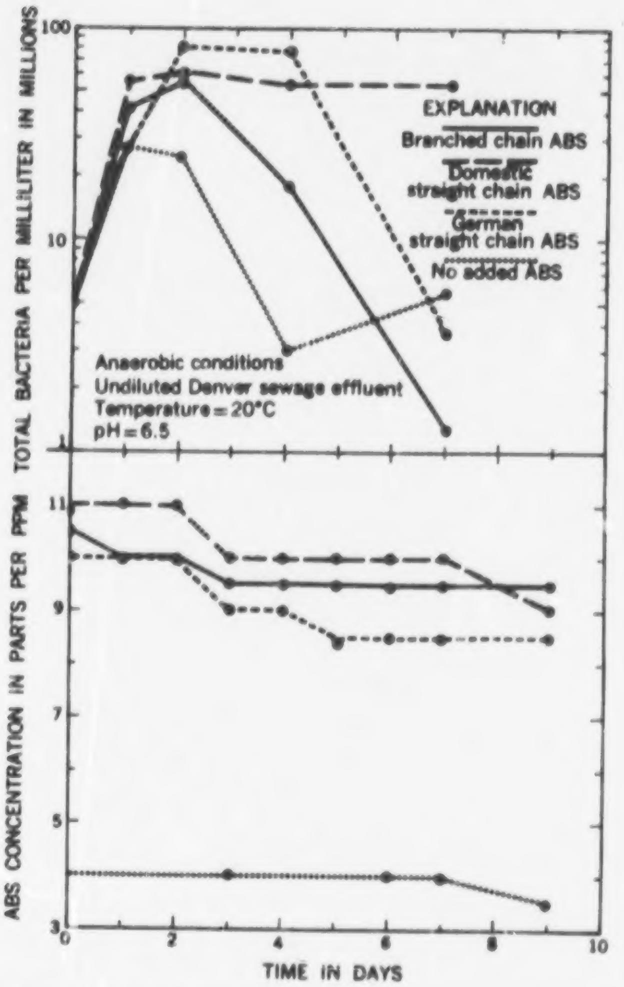


Figure 44. —Degradation of branched-chain and straight-chain ABS under anaerobic conditions at 20°C in undiluted river water.

Figure 44 shows the anaerobic breakdown of ABS in undiluted river water (initial total bacterial of 5,000,000 per ml) at 20°C. Under these conditions, neither type of ABS is significantly degraded. It is also evident that the extreme amount of bacterial growth must be attributed to nutrients in the water other than ABS.

Figure 45 presents data for solutions identical to those of Figure 36 but for aerobic conditions. Branched-chain ABS displays poor degradation properties even after one week. Both types of straight-chain ABS can be nearly totally degraded in aerated water in about one week. The effect of temperature increase on ABS degradation seems to increase both the rate and the total amount; however, part of this effect might be attributed to a much higher initial concentration of bacteria—nearly a three-fold increase as compared to the initial concentration at 10°C (aerobic conditions). The bacterial growth curves at 20°C seem to be normal except for the typical lag phase (acclimation time).

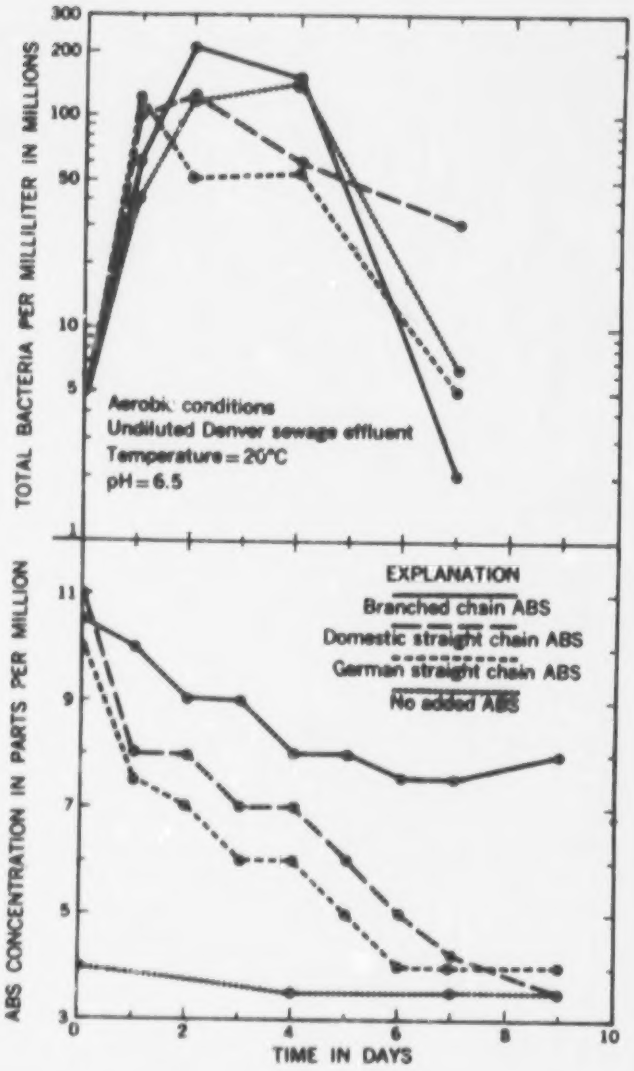


Figure 45. —Degradation of branched-chain and straight-chain ABS under aerobic conditions at 20°C in undiluted river water.

Figure 46 shows results of aerobic and anaerobic degradation of ABS at 35°C with initial total bacterial concentrations of 8400 per ml. Branched-chain ABS is extremely stable under aerobic or anaerobic conditions at low bacterial concentrations. Under anaerobic conditions, straight-chain ABS shows only modest amounts of degradation. Under aerobic conditions, domestic straight-chain ABS seems to degrade very rapidly and to a high degree of completion in about one week; the German material seems to degrade more slowly and less completely than the domestic ABS.

Figure 47 shows the results at 35°C with initial total bacterial concentrations of 1,300,000 per ml for aerobic and anaerobic conditions. Under anaerobic conditions increased concentration of bacteria will not produce enchanced amounts of ABS degradation as compared to

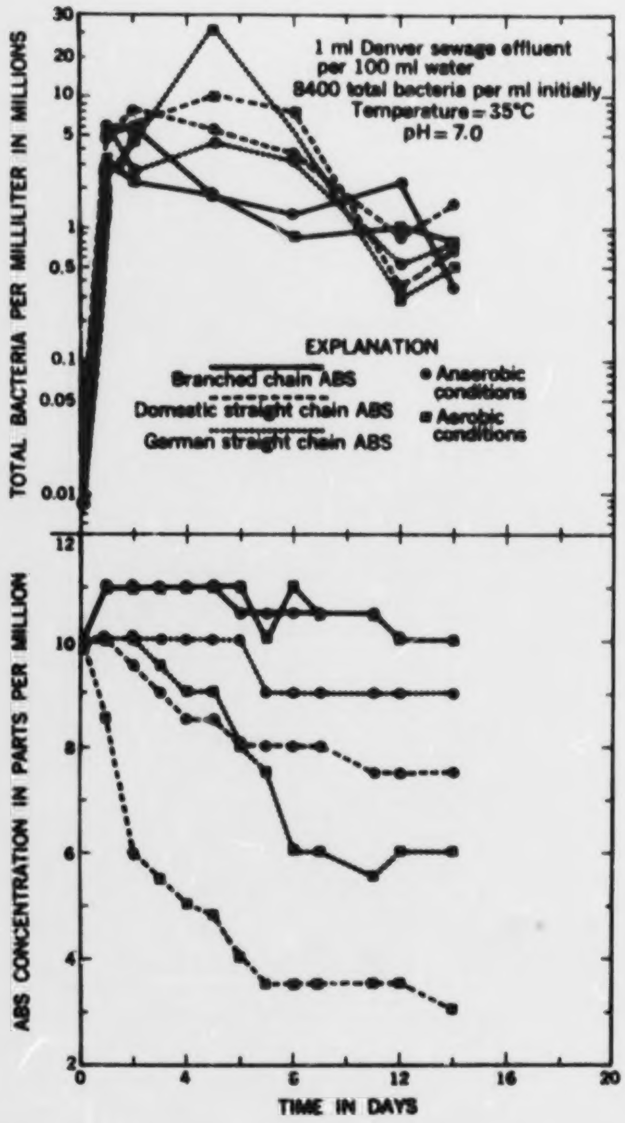


Figure 46. —Degradation of branched-chain and straight-chain ABS under aerobic and anaerobic conditions at 35°C in river water diluted 100 to 1.

the results of figure 38. Branched-chain ABS under aerobic conditions tend to approach degradation characteristics similar to straight-chain ABS for anaerobic conditions. High bacterial concentrations at 35°C increase the rate at which straight-chain ABS can be degraded; total degradation can be obtained in about 2 days.

Our study has shown that significant amount of straight-chain ABS or branched-chain ABS cannot be degraded under anaerobic conditions in the temperature range 10°C to 35°C; in all instances the rates are extremely slow and seem to be somewhat independent of both temperature and bacterial concentration. This aspect would seem to have some relationship between future considerations regarding

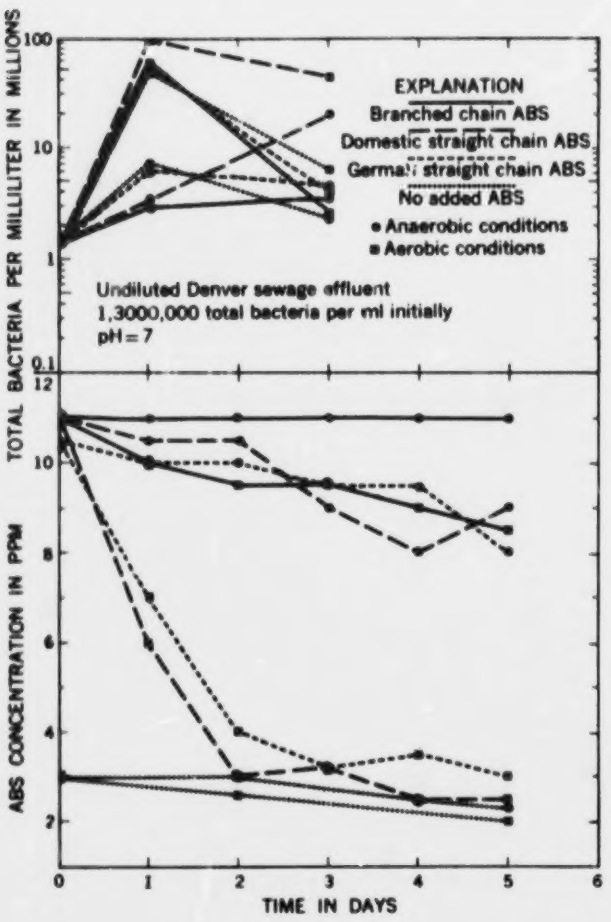


Figure 47. —Degradation of branched-chain and straight-chain ABS under aerobic and anaerobic conditions at 35°C in undiluted river water.

ground-water pollution by ABS. Assuming that newer types of ABS (straight-chain) may be employed in future detergents, it seems unlikely that anything approaching complete degradation would occur under anaerobic conditions. Thus, the discharge of septic tank effluents or cesspool wastes containing straight-chain ABS (assuming anaerobic enviroments) into the ground might still produce significant amounts of ABS pollution. It should be additionally stressed that, under anaerobic conditions, ABS and probably other organic constituents would be incompletely and very slowly biodegraded. The extent of organic degradation was not evaluated since total organics (COD-chemical oxygen demand) and aerobically degradable organics (BOB-biological oxygen demand) was not determined in our studies.

The degradation of branched-chain ABS in aerated river water can be achieved only to a limited extent regardless of bacterial concentrations up to about 1,000,000 per ml and temperature. However, the newer types of ABS (straight-chain) seem to be quite sensitive to bacterial concentration and temperature with regard to degradation in aerated water; both increase in bacterial concentration and temperature tend to accelerate degradation. Our results at 35°C indicate that water containing about 11 ppm of "soft" ABS can be nearly completely degraded in 2 days; Roberts (1961) showed that aerated sewage effluent containing 14.75 ppm of "soft" ABS could also be nearly completely degraded in 2 days at 37°C, indicating good agreement between the two independent studies. Many other investigators have shown that newer types of ABS can be degraded to a high degree in a few hours by sewage plants employing an activated-sludge process or at longer periods of time in river water. For those sewage plants employing only primary treatment, significant amounts of newer types of ABS would probably be discharged with the sewage effluent. Under these conditions, it can be inferred from this study that additional breakdown of ABS may be achieved in aerated surface water. The rate of breakdown in surface water would of course be dependent on bacterial concentration and temperature. The temperature effect would seem to indicate that degradation should be more rapid in the summer than in cooler winter water.

Thus, foaming and other problems created in sewage plants and aerated surface water should be drastically improved if "soft" ABS is substituted for "hard" types; under anaerobic conditions pollution of water by even "soft" ABS will probably continue to certain extent, unless the discharge into the ground takes place under aerobic conditions.

The writers wish to express their thanks and cooperation from the following companies for supplying samples of ABS used in this part of our study:

(1) Monsanto Chemical Company (domestic straight-chain ABS).

(2) Chemische Werks Hüls (German straight-chain ABS) and

(3) California Research Corporation (branched-chain ABS).

ADSORPTION OF SURFACTANTS AND DETERGENT BUILDERS ON SOLID MINERAL SURFACES

When household or sewage waste water containing incompletely degradable surfactants in detergents infiltrates into the ground from rivers, streams, cesspools, holding ponds, or septic tanks, pollution of ground water may occur. Because natural soils (greensand marl, weathered basalt, Brighton sandy loam, weathered hornblende schist, Adobe, loess, muck, and Long Island aquifer sand) and therefore, minerals (glauconite, goethite, gibbsite, kaolinite, illite, and montmorillonite) comprising these soils may serve as decontamination media for removal of the surfactant (ABS) from waste water, a study was made of the adsorption of ABS on these substances. Data are also compared to those obtained for ABS adsorption on the synthetic adsorbents, activated charcoal and "Baymal" (colloidal alumina).

Previous studies on adsorption of ABS on natural materials have been reported but the differences in analytical techniques, experimental conditions, and materials studied do not justify comparison of data on an equivalent basis. Table 17 shows the adsorption of ABS on various materials from solutions containing 5 ppm. Jenkins and Klein (1961) found that sands and sandy loams adsorbed from 1.4 to 22.1 µg ABS per g (micrograms ABS per gram) solid from solutions containing 1.0 ppm. Ewing, Lefke, and Banerji (1960) reported that the "20-30 Ottawa Sand" adsorbed about 3.8 µg ABS per g sand from solutions containing 10 ppm. The same investigators (Ewing and Banerji, 1962) suggest that this adsorption becomes much greater if active bacteria are present as a gel on these sand grains. Robeck (1961) reported that similar sands showed adsorption capacities that ranged from 3.0 to 20.0 µg per g dependent upon the surface area of the sand for solutions containing 10 ppm of ABS.

Table 17.—Adsorption of ABS on mineral surfaces (Renn and Barada, 1959)

Material	Adsorption Capacity (µg ABS per g solid)
Natural stream siet	25,000
Talc	2,000
Precipitated CaCO$_3$	1,400
China clay	1,200
Diatomite	660
Silica gel	650

In our study a radiochemical tracer technique was combined with membrane dialysis to study the effects of varying ABS concentration, alkyl chain length, pH, the additives phosphate and carboxymethylcellulose ions, and salt content (NaCl, CaCl$_2$, or AlCl$_3$) on ABS adsorption by soils, natural minerals, and synthetic adsorbents.

The ABS employed consisted of branched-chain material tagged with sulfur-35 containing either 12 carbon atoms (dodecyl ABS) or 15 carbon atoms (pentadecyl ABS).

The adsorbents used were kaolinite (Dry Branch, Georgia), illite (American Petroleum Institute No. 35, Fithian, Illinois), montmorillonite (American Petroleum Institute No. 26, Clay Spur, Wyoming), goethite (Biwabek, Minnesota), gibbsite (Minas Gerais, Brazil), glauconite (Hazlet, New Jersey), and a variety of representative soil types as mentioned in the first paragraph of this section of the report. The synthetic adsorbents used were unground 30 mesh activated charcoal (Nuchar C190, West Virginia Pulp and Paper Company) and Dupont Company "Baymal" (colloidal alumina-Lot Number 61-36).

All adsorbents except the soils and synthetics were used without treatment other than sizing at 2µ (microns) with "Calgon" [(NaPO$_3$)$_6$] as the dispersant; additional sizing was carried out with an ultracentrifuge producing material in the size range 0.2 to 2.0 µ. The natural soils were used on an as received basis with characteristics presented in the following section on "Column Studies." "Baymal" is a positively charged colloidal alumina in acid solution; it consists of fibrils of boehmite (AlOOH) approximately 5 mµ in diameter and 100 to 150 mµ in length. "Baymal" has a surface area of 274 square meters/g, a pore diameter of 77 angstroms, and a pore volume of 0.53 cc/g. Activated carbon is quite variable in physical dimensions. In our study the material used was unground, 30-mesh. Particle diameters may range from less than 100 angstroms to as much as 5000 angstroms; average open-pore volumes contain about 0.1 to 0.3 cc/g, and have a total surface area of as much as 1000 square meters/g with pore diameters of about 20 angstroms.

Table 18.—*Analytical data on clays.*

Clay	Kaolinite	Illite	Montmorillonite
C. E. C.[1]	3.5	25.0	99.0
pH of suspension[2]	6.9	6.8	7.5
Surface area (m^2/g)	20	78	109
Typical chemical analyses (percent weight):			
SiO_2	45.00	52.61	60.25
Al_2O_3	38.21	24.82	18.17
Fe_2O_3	.25	4.10	2.82
FeO	.02	.25	.02
MgO	.40	2.26	2.86
CaO	.42	.31	.20
Na_2O	.30	.34	1.55
K_2O	.50	5.71	.27
TiO_2	.52	.61	.11
$(+)H_2O$	13.35	7.93	6.75
L. O. I.[3]	14.01	8.81	14.78

[1] Cation exchange capacity in milliequivalents per 100 g of solid clay material.

[2] pH of a suspension containing 200 milligrams of clay per 35 cc of distilled water.

[3] Loss on ignition.

The cation-exchange capacity, pH of the clay suspension, surface area (determined by low temperature nitrogen gaseous adsorption with an apparatus of standard design, Emmett, 1942), and typical chemical analyses of the clays are listed in table 18. The goethite and gibbsite were essentially pure varieties of $Fe(OH)_3$ and $Al(OH)_3$, respectively, purchased from Wards Mineral Collection. Glanconite was a highly weathered variety of the New Jersey "greensand" and was not analyzed. Generalized formulas to represent the minerals are:

Kaolinite

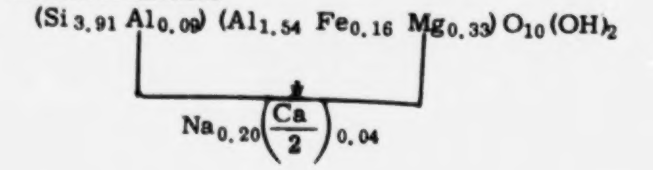
$Al_2(Si_2O_5)\ (OH)_4$

Illite

$$[K_{0.5-0.7}(H_3O)_{0-0.3}]_{0.5-1.0}\ [Al_{2.0-1.7}\ Mg_{0-0.3}]_{2.0}$$

$$[Si_{3.3-3.6}\ Al_{0.4-0.7}]_{4.0}O_{10}\ (OH)_2$$

Montmorillonite



$$\underbrace{(Si_{3.91}\ Al_{0.09})\ (Al_{1.54}\ Fe_{0.16}\ Mg_{0.33})}_{Na_{0.20}\left(\frac{Ca}{2}\right)_{0.04}}O_{10}(OH)_2$$

Glauconite

complex, hydrous, alumina, iron (Fe_2O_3 and FeO), magnesium, potassium silicate

Gibbsite

$Al\ (OH)_3$

Goethite

$Fe\ (OH)_3$

The experimental set-up is shown in figure 48. In each experiment 10 ml of an adsorbent suspension at a concentration of 200 mg per 10 ml of deionized-distilled water were sealed in a sausage casing (membrane tube-Visking Corporation, Nojax, Size 18) and placed in a 2 ounce polyethylene bottle. Ten ml of a radioactive ABS ^{35} (either dodecyl or pentadecyl at an original specific activity of one millicurie per millimole) solution of different concentrations with or without other anions and cations were then pipetted into the bottle around the adsorbent (external to the sausage casing) and the capped bottle was placed in a constant temperature (25°± 1°C) agitated water bath. The total volume of the liquid phase was 20 ml and the total weight of the clay was 200 mg. The sausage casing functioned as a molecular sieve, being permeable to ABS ions but impermeable to the adsorbent. In time various amounts of ABS would equilibrate with the adsorbent surface.

The solutions were sampled in duplicate 1-ml aliquots and evaporated to dryness on planchets. The samples were then counted in a sheilded end-window Geiger counter. The counting rates of the test samples were compared to standards containing microgram amounts of ABS tagged with sulfur-35. The total number of counts for both the standards and test samples were corrected for background of about 28 counts per minute. The

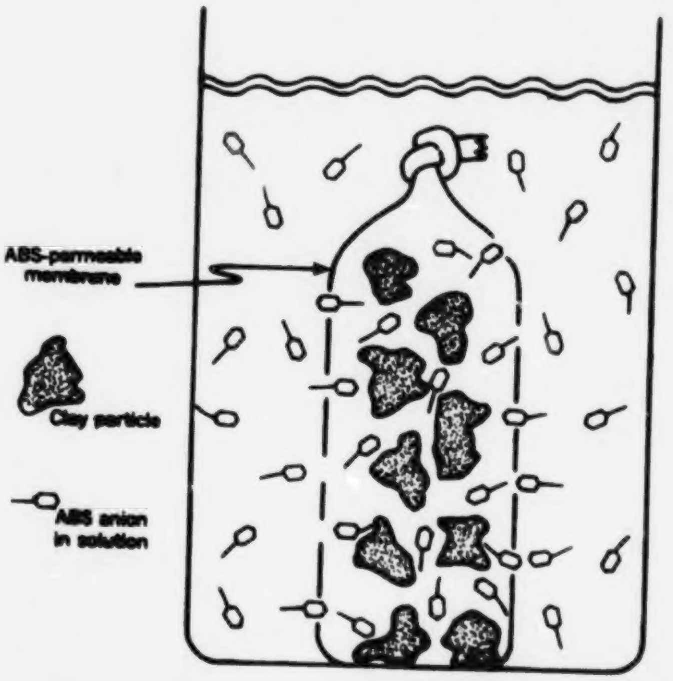


Figure 48.—Detail of experimental set-up for studies ABS adsorption.

amount of ABS adsorbed per gram of adsorbent can be calculated from the relationship

$$A_k = \frac{(C_s - C_t)}{C_s W_k} V K_s \qquad (67)$$

where

A_k = micrograms ABS adsorbed per gram of absorbent.

C_s = the counting rate (counts per second) of 1 ml of evaporated ABS-35 of known starting concentration (K_s) corrected for background.

C_t = the counting rate (counts per second) of 1 ml of evaporated test sample solution corrected for background.

K_s = ABS-35 concentration (parts per million at the beginning of an experiment.

W_k = weight of clay in grams.

V = volume of water used in ml.

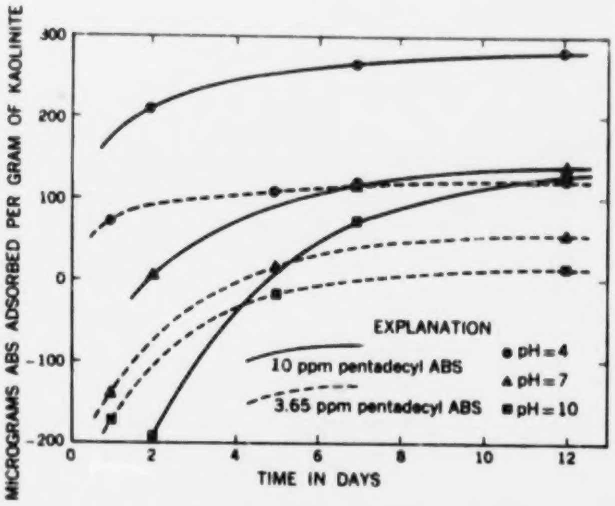


Figure 49. —Influence of pH, ABS, concentration, and time on adsorption of ABS by kaolinite.

Figure 49 shows typical effects of ABS concentration on uptake by kaolinite and other clays at various pH. The data indicate that ABS adsorption from solution increases with increase in ABS concentration. Figure 50

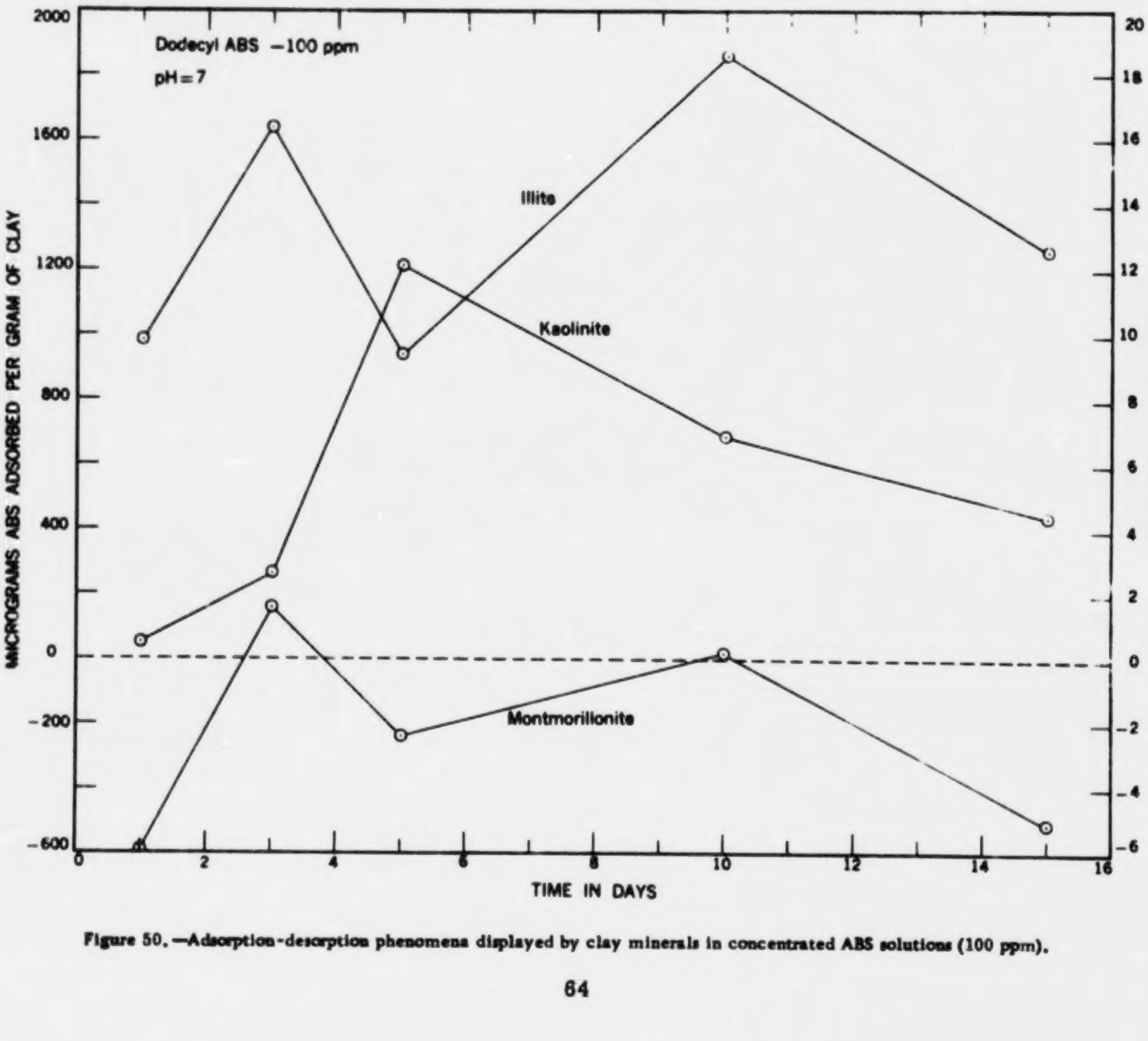


Figure 50. —Adsorption-desorption phenomena displayed by clay minerals in concentrated ABS solutions (100 ppm).

shows the manner in which ABS is adsorbed and subsequently desorbed (physically) on various clays with time in concentrated (100 ppm) solutions of ABS. The most obvious effect is with respect to montmorillonite adsorption; at this concentration (100 ppm) ABS fluctuates between high amounts of negative adsorption to slightly positive values, probably as a result of the highly negative surface of montmorillonite at a pH of 7 causing repulsion of ABS at the surface. Illite and kaolinite show intensive amounts of adsorption-desorption effects during various periods of equilibration. Thus, in concentrated ABS solutions, it is difficult to adsorb ABS on clays without desorption. Desorption on soils has also been observed by other investigators (Klein and others, 1961). On application of a more dilute solution of ABS to soils which had originally adsorbed ABS from more concentrated solutions, these investigators observed that significant amounts of ABS could be desorbed indicating additional allusion to the weakness with which ABS is adsorbed. Figure 51 shows a Freundlich plot for adsorption of ABS on various minerals. The Freundlich isotherm is usually employed to describe the manner in which molecular or ionic species are removed from solution by adsorption on solids (adsorbents) and usually takes the form

$$\frac{X}{M} = KC^{1/n} \qquad (68)$$

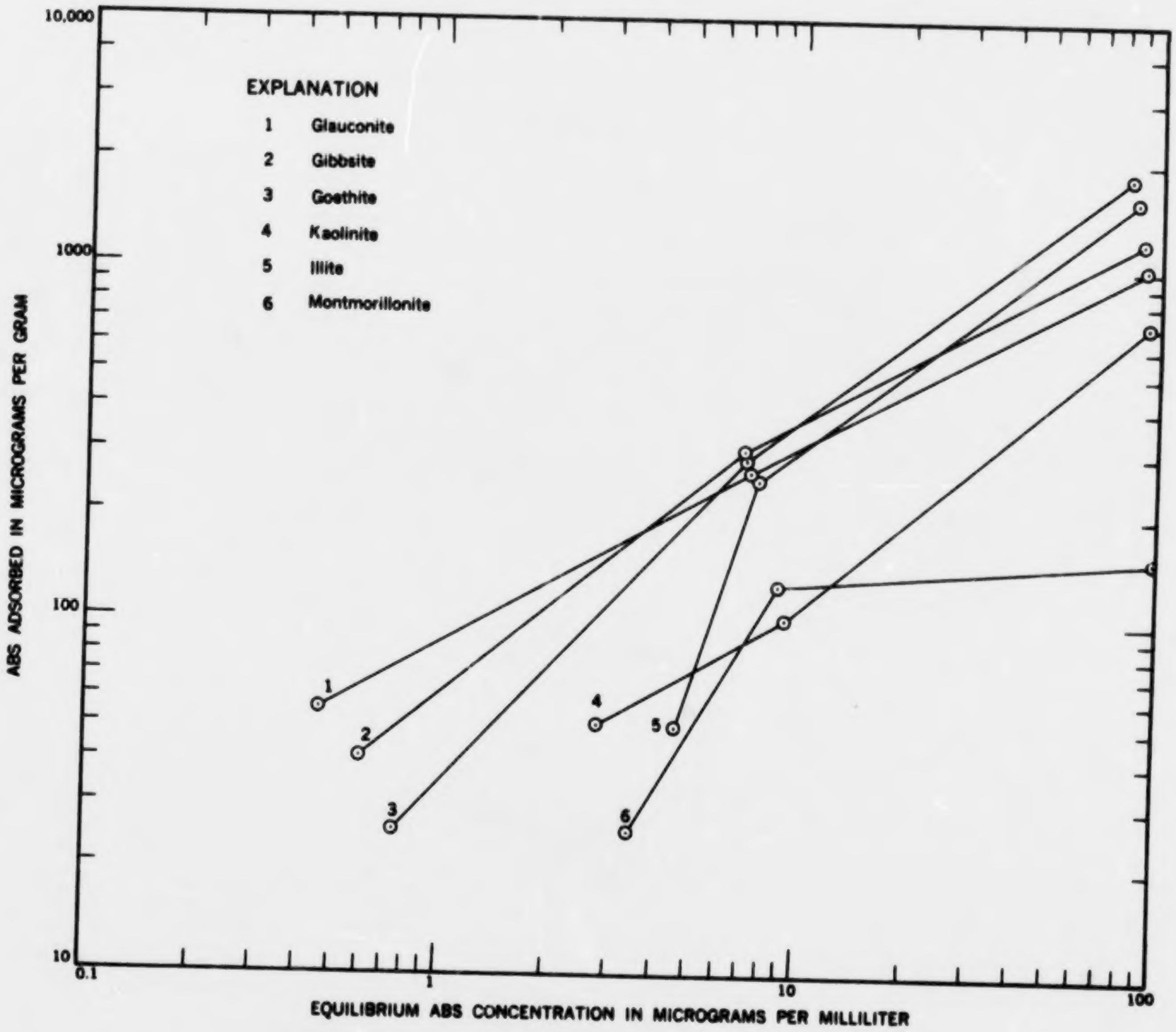


Figure 51.—Freundlich plot for adsorption of ABS on various minerals.

where

X = weight of solute adsorbed.

M = unit weight of adsorbent.

K and n = constants dependent upon the type of adsorbent.

C = concentration of the solute in solution at equilibrium.

or written in logrithymic form as

$$\log \frac{X}{M} = \log K + \frac{1}{n} \log C \tag{69}$$

where the constants can be evaluated from a plot of $\log \frac{X}{M}$ against $\log C$ giving a slope of $\frac{1}{n}$ and $\log K$ is the intercept at $\log C = 0$. Most of the adsorption data give reasonable and expected straight line relationships except montmorillonite at high ABS concentrations probably resulting from excessive amounts of negative adsorption at this level (figure 50). The equations for evaluating ABS adsorption on the various minerals based on figure 51 and equation 68 between 1 and 100 ppm are:

Glauconite

$$\frac{X}{M} = 86\,C^{0.56} \tag{70}$$

Gibbsite $$\frac{X}{M} = 62\,C^{0.69} \tag{71}$$

Goethite $$\frac{X}{M} = 38\,C^{0.91} \tag{72}$$

Illite $$\frac{X}{M} = 30\,C^{0.90} \tag{73}$$

Kaolinite $$\frac{X}{M} = 22\,C^{0.75} \tag{74}$$

Montmorillonite

$$\frac{X}{M} = 15\,C^{0.63} \tag{75}$$

Although equations (70) to (75) indicate a general increase in ABS adsorption with increase in ABS concentration, no information regarding the adsorption mechanism (monolayer or multilayer adsorption) is revealed. Such data may be determined by the well-known Langmuirian adsorption isotherm which is not treated in this report. Recent studies (Chao, 1960) indicate that the adsorption of $S^{35}O_4$ on soils high in free iron and free aluminum oxides at S concentrations 5 to 500 ppm produced Freundlich equations in the range

$$\frac{X}{M} = 15.21 - 23.99\,C^{0.483-0.576} \tag{76}$$

suggesting that surfactant sulfur (sulfonate) is more readily adsorbed on materials high in Gibbsite or Goethite (equations 71 and 72) than sulfate sulfur.

In figure 52 the adsorption of ABS on clays is compared to that on the synthetic adsorbents "Baymal" and activated charcoal. The data show that clay minerals are inefficient adsorbents in comparison to the synthetic materials studied. Activated carbon displays an extremely high affinity for ABS with an adsorption capacity of over 1000 μg per g of carbon. These large disparities in adsorption between natural and synthetic materials can be attributed to the dynamic positive and large pore diameter for "Baymal" and to the high internal and external surface area for activated carbon. Though clays are inefficient adsorbents for the removal of ABS, the exorbitant cost of "Baymal" or activated carbon makes synthetics unattractive at the present time.

The influence of length of the alkyl chain on adsorption is shown in figure 53. As the length of the alkyl chain is increased from 12 to 15 carbon atoms, as much as 2 to 4 times ABS can be removed by pentadecyl ABS as compared to dodecyl ABS; the change in amount of removal depends on the type of clay. The dependence of adsorption on molecular weight, as found in this study, has been observed by others. McAtee (1959) indicated that sodium can be replaced in montmorillonite more easily by large quaternary compounds than by substances of lower molecular weight such as primary amines. Also, Greenland and others (1962) showed that peptide adsorption on montmorillonite increases as the molecular weight of the peptide increases. Similarly, Smith and Bader (1961) demonstrated that the association of amino acids, dibasic acids, and carbohydrates with montmorillonite depends largely upon their molecular weight. Thus, these data indicate that the free energy of adsorption, including physical adsorption, increases as the molecular weight of the adsorbate increases.

Complex phosphates such as tetrasodium pyrophosphate ($Na_4P_2O_7$) or pentasodium tripolyphosphate ($Na_5P_3O_{10}$) are essential components in detergents. In waste water these phosphates are probably biologically degraded (Cohen, 1959) or hydrolyzed

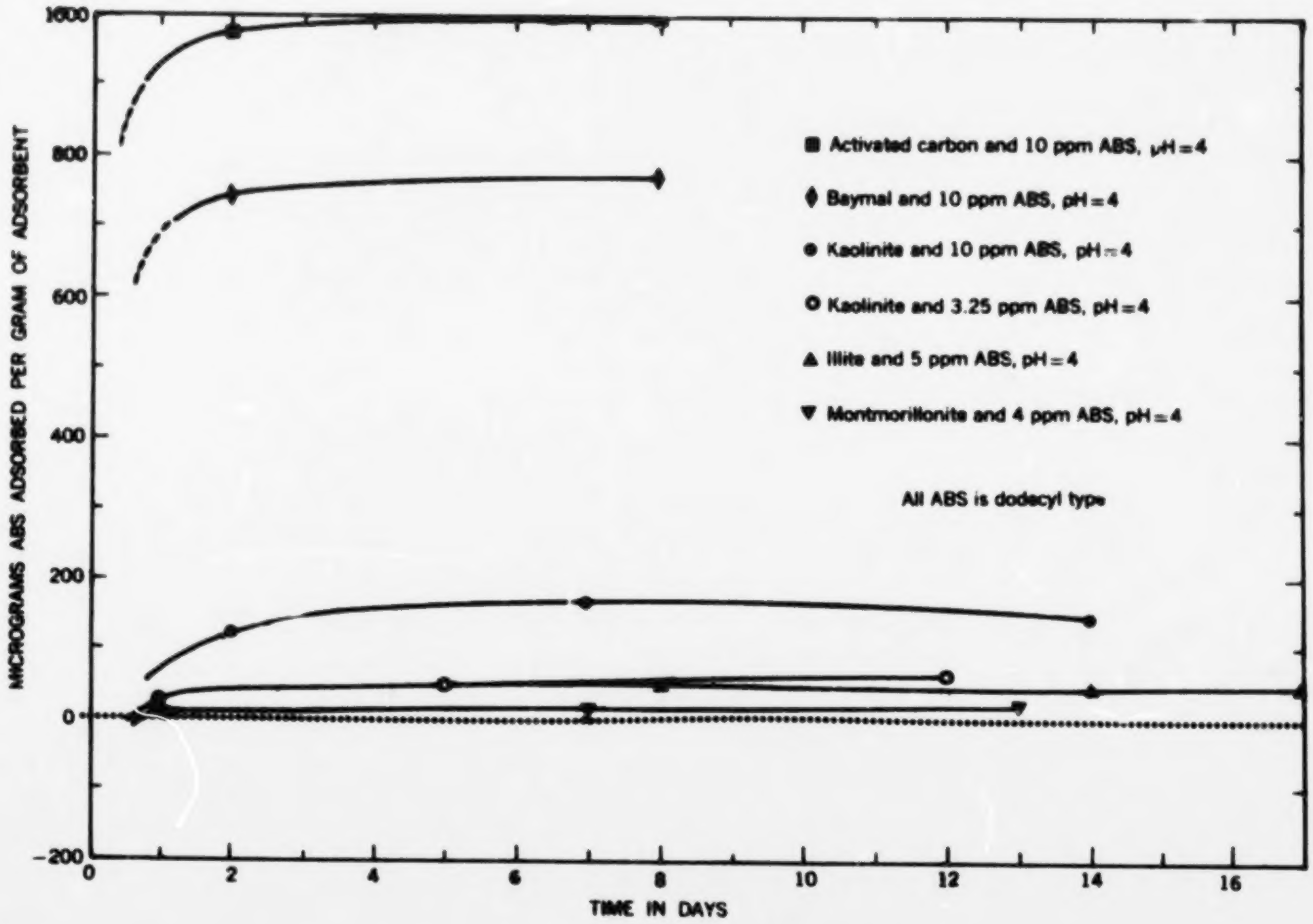


Figure 52. —Comparison of ABS adsorption on clays and synthetic adsorbents.

(Morgan and Engelbrecht, 1960) to orthophosphates. The specific anionic form of orthophosphate in water depends upon the pH of the water. The ionizations of H_3PO_4 have been reviewed by Pitzer (1937) and are listed as

$$H_3PO_4 = H^{+1} + H_2PO_4^{-1} \quad K_1 = 7.5 \times 10^{-3} \quad (77)$$

$$H_2PO_4^{-1} = H^{+1} + HPO_4^{-2} \quad K_2 = 6.2 \times 10^{-8} \quad (78)$$

$$HPO_4^{-2} = H^{+1} + PO_4^{-3} \quad K_3 = 10^{-12} \quad (79)$$

At pH 4, $H_2PO_4^{-1}$ predominates, but the solution contains a minor amount of H_3PO_4; at pH 7, mixtures of HPO_4^{-2} and $H_2PO_4^{-1}$ are in solution. At pH 10, HPO_4^{-2} predominates, but the solution contains a minor amount of PO_4^{-3}. Because these anionic species may compete with ABS for adsorption by clays, solutions containing orthophosphate were used to study ABS adsorption by clays.

Figure 54 shows typical effects of pH, equilibration time, and phosphate on ABS adsorption using montmorillonite as an example. Test solutions contained 5 ppm of dodecyl ABS and 10 ppm of orthophosphate. In neutral (pH 7) and in alkaline (pH 10) solutions, small amounts of ABS are negatively adsorbed for as long as about two weeks, at which time positive adsorption begins. In acid solutions (pH 4) the amount of ABS adsorbed initially increases with time; then, after about 9 days, desorption occurs for about 1 week, after which apparent equilibrium is achieved. Negative adsorption occurs significantly at pH 7 and pH 10; this effect is to be expected at a pH displaying little or no anion adsorption and can be calculated from Gouy theory. At pH 4, where anion adsorption seems to occur, this effect was not observed. Effects of anionic negative adsorption on clays have been observed by others (Mattson, 1931; Schofield, 1949; and Bolt and Warkentin, 1958). Because the amount of ABS adsorbed from solutions containing both ABS and phosphate ions is greater than that adsorbed from solutions containing only ABS (figures 53, 54) phosphate fixation probably occurs on the clay either before or simultaneously with ABS adsorption. Some investigators (Coleman, 1944;

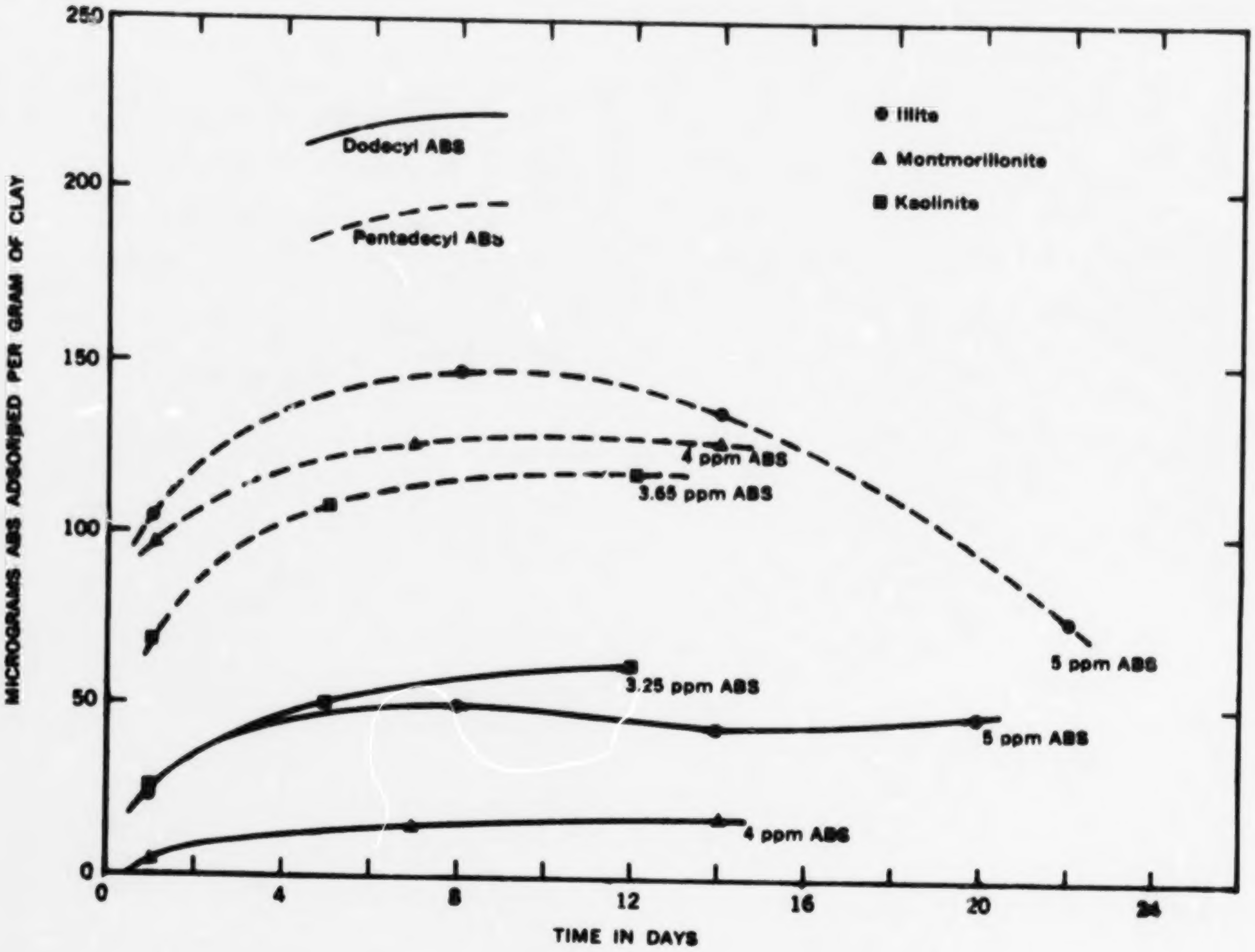


Figure 53. —Influence of length of the alkyl chain and time on adsorption of ABS on various clays.

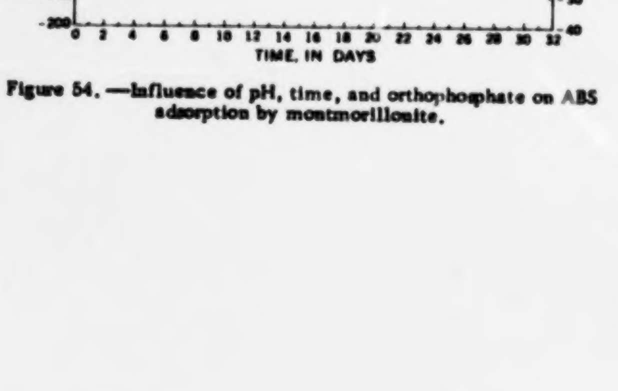


Figure 54. —Influence of pH, time, and orthophosphate on ABS adsorption by montmorillonite.

Chatterjee and Dalta, 1951) suggest that this fixation results from active iron and aluminum oxides in clays. Others (Murphy, 1939; Scarseth, 1935; and Stout,.1939) believe that phosphate ions exchange with hydroxyl ions at the edge of the crystal lattice. Ravkovitch (1934) proposed that phosphate becomes fixed by an H_2PO_4-Ca-clay linkage. Low and Black (1948) attribute phosphate fixation to aluminum released by decomposition of the clay. Ellis and Truog (1955) indicated that phosphate becomes fixed by the formation of calcium phosphate complexes. Aluminum and phosphate in dilute solution at low pH may form complex cations such as $AlHPO_4^{+1}$, $AlH_2PO_4^{+2}$, and $Al(H_2PO_4)_2^{+1}$ (Salmon and Wall, 1958). Because ABS uptake increases with phosphate in solution at pH 4, phosphate probably does not compete with ABS for adsorption sites. In this study the heteroionic nature of the clay surface could have contributed aluminum to the solution for the formation of an aluminum phosphate ion; these large ions might have combined with ABS to form an aluminum phosphate—ABS complex which could have been adsorbed by the clay. In addition to this type of a mechanism, any of the above might be used to explain phosphate fixation on clays before or simultaneously with ABS adsorption.

Figure 55 shows the influence of pH, and other anionic species (phosphate and carboxymethylcellulose) on removal of ABS by various clays. The various forms of phosphate to be expected in solution were given previously; carboxymethylcellulose can be represented by the general form ($R\text{-}O\text{-}CH_2COO$). The most obvious effect for all clays is that ABS adsorption decreases markedly with increase in pH between 4 and 10. The pH effect can be explained on the basis of the increased amount of positive sites on the clay surface in acid solution, thus, facilitating anionic adsorption. Normally (pH 7) clay is negatively charged in solution from the severance of silicon-oxygen, aluminum-oxygen, or aluminum-hydroxyl bonds; some types of clays (illite and montmorillonite) are negatively charged in part from isomorphous replacement of Al^{+3} for Si^{+4} in the tetrahedral layer and Mg^{+2} for Al^{+3} in the octahedral layer. Impurities in clays such as iron or aluminum hydroxides or organic matter may also influence charge distribution on clay surfaces. Because hydrogen ions function as potential determining ions at low pH, enhanced removal of anionic ABS is to be expected under these conditions. Other investigators have also indicated that anion adsorption on clay minerals is dependent on pH (Schofield, 1949; Schofield and Samson, 1953; Street, 1956; and Holtzman, 1962). When phosphate is in solution with ABS, a greater amount of ABS is adsorbed (compare kaolinite curves); this effect is nearly equal for illite and kaolinite, which are both greater than for montmorillonite. When both phosphate and carboxymethylcellulose are in solution with ABS,

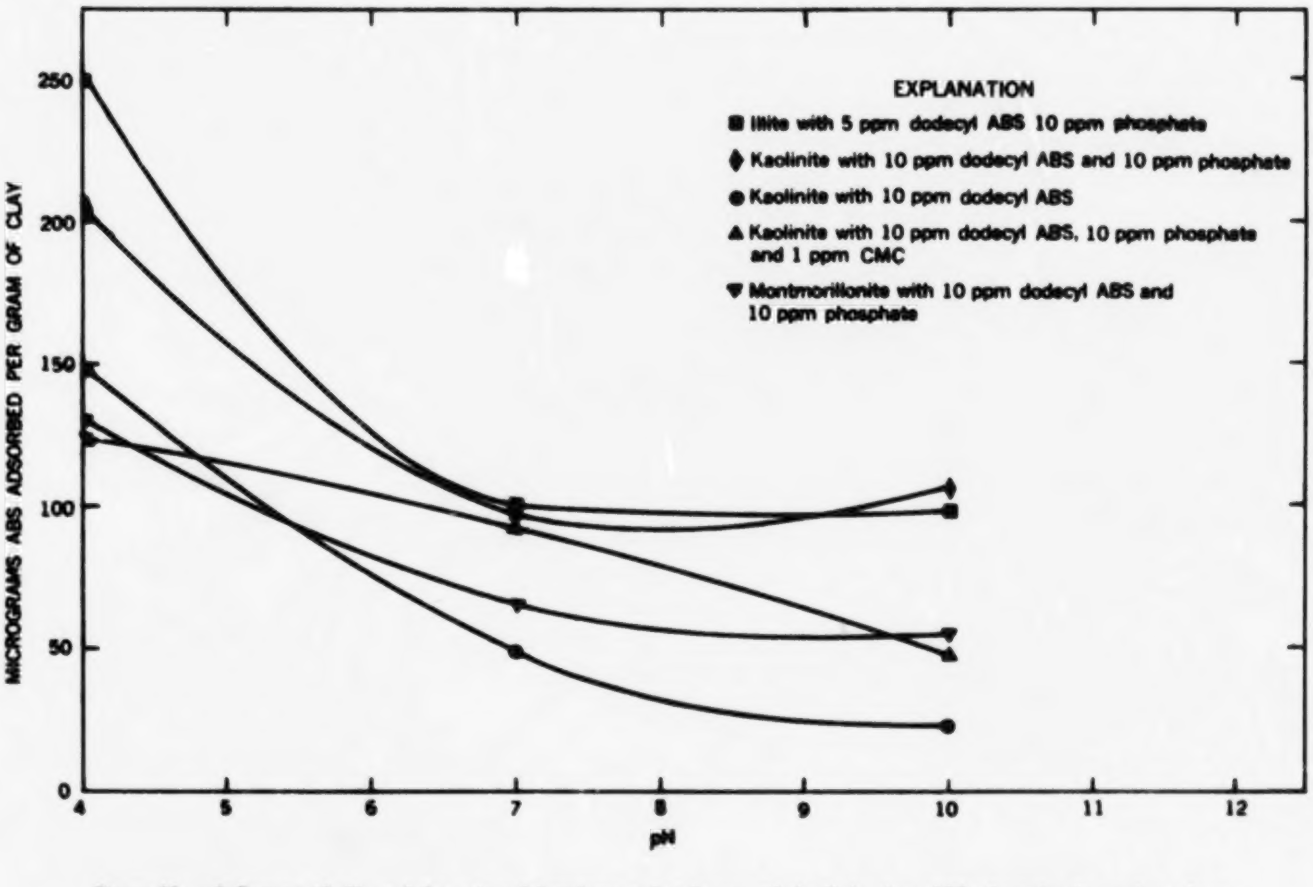


Figure 55.—Influence of pH, and the anions (phosphate and carboxymethylcellulose) on ABS adsorption by various clays.

little change in ABS adsorption by kaolinite was observed. Therefore, neither phosphate nor carboxymethylcellulose ions seem to interfere (compete with) ABS for adsorption sites on clay surfaces. The reasons for enhanced adsorption of ABS with phosphate in solution were given previously.

Because dissolved salts may be present in large concentration in waste solution, the removal of ABS by clay minerals was also studied at various pH with different concentrations of NaCl, $CaCl_2$, and $AlCl_3$ in solution. Table 19 shows the effects of pH, type of salt, and amount of salt on ABS adsorption by kaolinite. The data represent increase in ABS adsorption for solution containing about 0.01 moles per liter of various chlorides and 4 ppm of ABS as compared to solutions that contained only 4 ppm of ABS (no salt). Monovalent and divalent chloride salts seem to increase ABS adsorption equally well for the pH range 4 to 10. The trivalent salt ($AlCl_3$) causes much greater increase in adsorption, especially in the pH range 4 to 7.

Table 19.—Effect of various salts on ABS adsorption by kaolinite (Wayman and others, 1963–F)

pH		Percentage increase in ABS adsorbed
	NaCl, 584 ppm	
4		40
7		30
10		50
	$CaCl_2$, 952 ppm	
4		35
7		50
10		60
	$AlCl_3$, 1,333 ppm	
4		175
7		200
10		75

Figure 56 shows the effects of salt concentration, valence, and pH on ABS adsorption by montmorillonite. ABS adsorption seems to

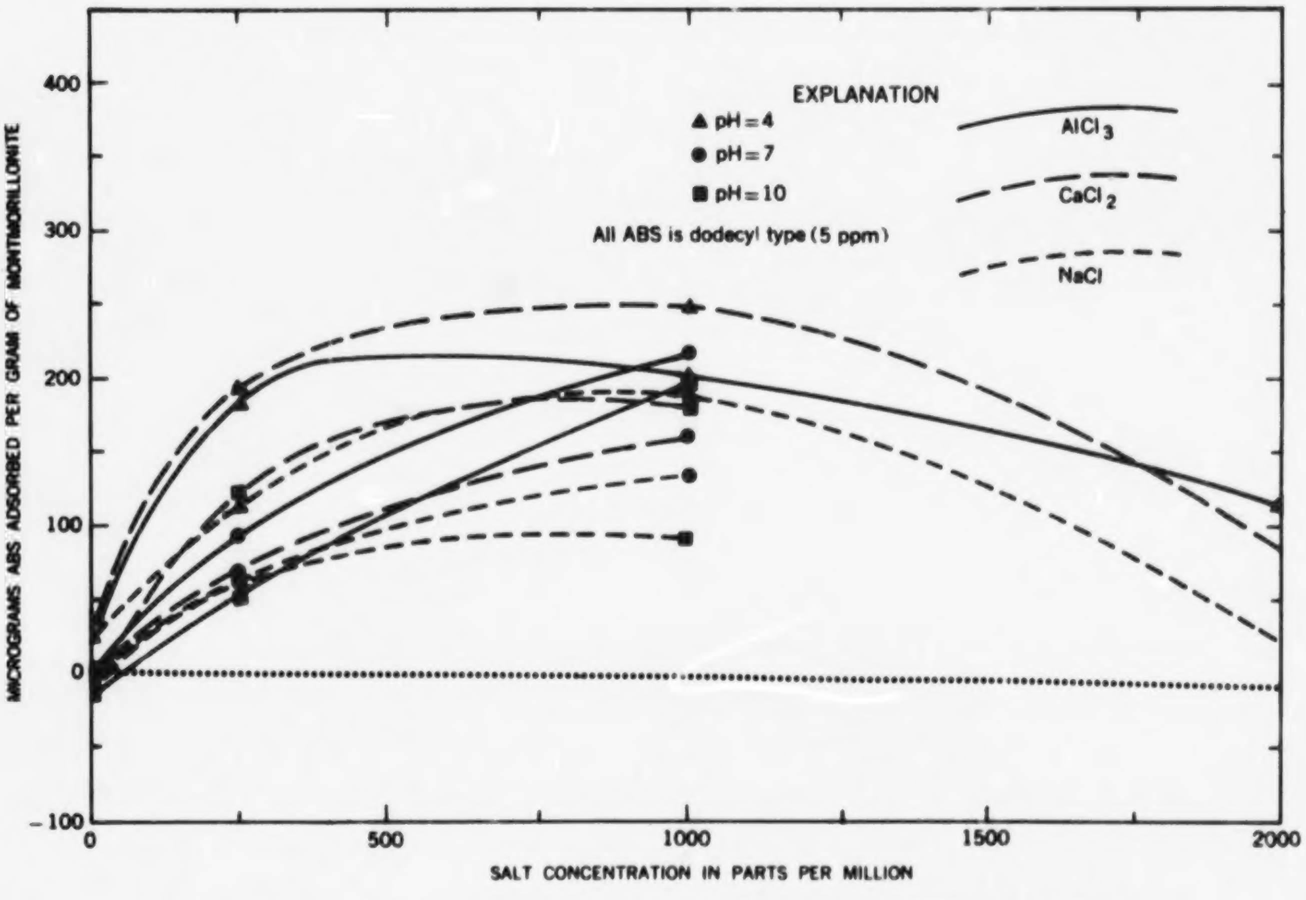


Figure 56.—Influence of salt concentration, valence, and pH on adsorption of ABS by montmorillonite.

be dependent on both pH and type and amount of salt; for solutions containing 5 ppm of ABS adsorption increases with decrease in pH and increases with increase in amount of salt up to about 1000 ppm; at higher salt content adsorption seems to decrease (between 1000 ppm and 2000 ppm). The effects for divalent and trivalent salts are similar—both being greater than for NaCl.

Figure 57 shows the effects of salt concentration, valence, and pH on adsorption of ABS by illite. These results are similar to those for montmorillonite but the total amount adsorbed generally exceeds that for montmorillonite, especially at low pH. Increased ABS adsorption parallels increase in salt content and decrease in pH. In acid solution (pH 4), increase in adsorption can be correlated with cationic charge where $Al^{+3}>Ca^{+2}>Na^{+1}$. All the data listed in table 19 and points plotted in figures 56 and 57 represent equilibrium adsorption values ranging in time from 5 to 10 days.

No single mechanism can be used to account for increased adsorption or removal of ABS when ionic salts are in solution. Several physico-chemical phenomena seem consistent in terms of interpretation of these results such as:

(1) possible lowering of the critical micelle concentration (CMC)

(2) formation of smaller micelles below the normal CMC

(3) the effect of the Schulze-Hardy rule on CMC and

(4) adsorption of ABS as an aluminum-hydroxy-ABS complex in acid solution.

The CMC is important to adsorption and other physico-chemical properties because it represents the concentration for optimum activity of a surfactant (Preston, 1948). Thus, if wetting and adsorption at a solid-liquid interface are influenced, at least in part by the CMC,

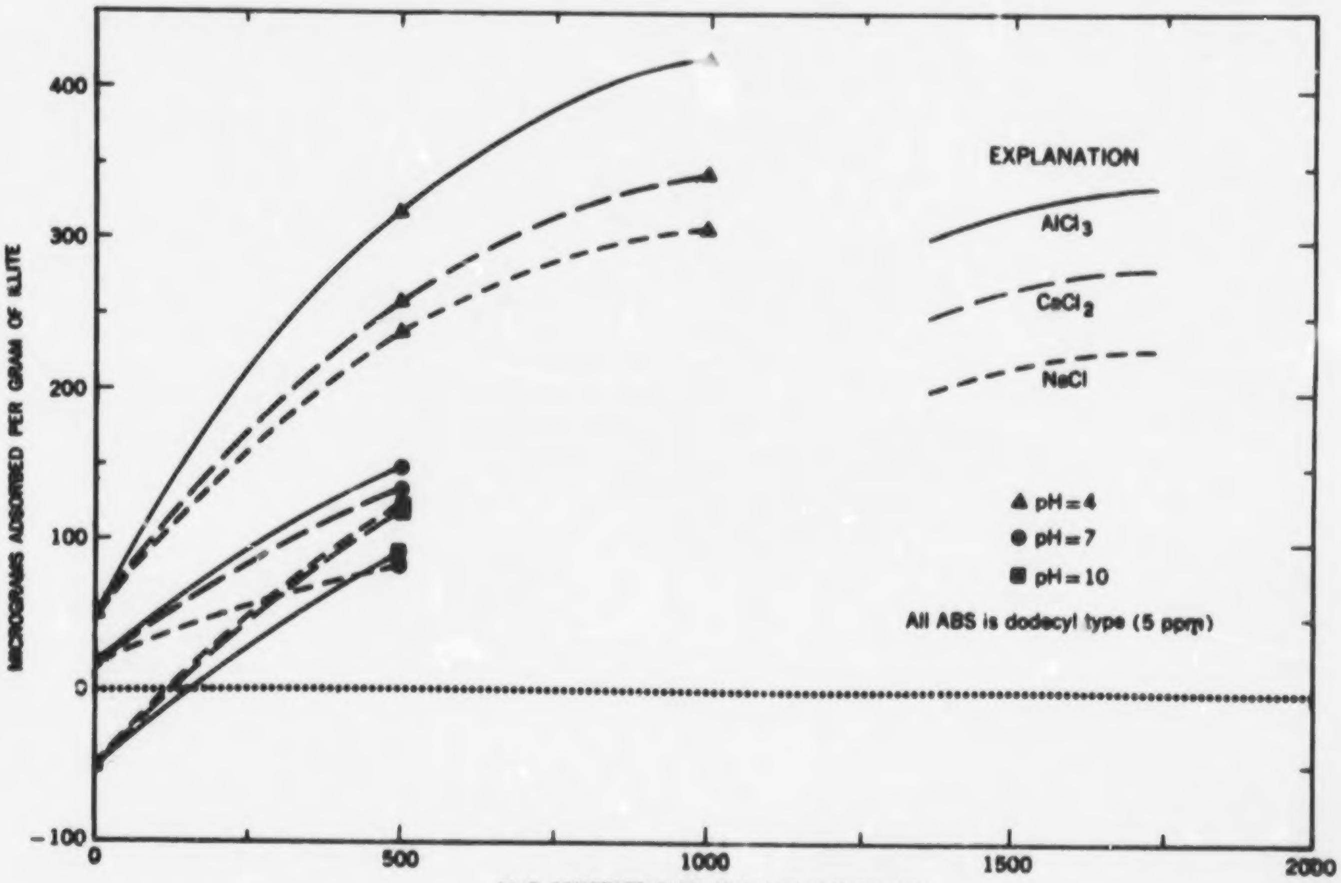


Figure 57.—Influence of salt concentration, valence, and pH on adsorption of ABS by illite.

then this parameter may be significant to adsorption of ABS on solid surfaces. The critical micelle concentration for solutions containing branched-chain dodecyl ABS has been determined as about 1000 ppm (Wayman, 1963-b). Other investigators suggest that surfactant micellar aggregation may occur below the CMC (McBain, 1950; and Winsor, 1956). If salts are in solution the concentration for micellar association can be decreased (Corrin and Harkins, 1947; and Harris, 1958). The Schulze-Hardy rule indicates that the amount of salt necessary to cause micellar association or colloid coagulation depends on the cation charge of the salt. This effect was observed by Lange (1951). For surfactant solutions Na^{+1} and Ca^{+2} behave as counter ions in lowering of CMC (Prins, 1955); however, Powney and Addison (1937) indicate that Fe^{+3} and Al^{+3} are less effective on micellar association than Ca^{+2} as a result of ionic hydration. At the low surfactant concentration used in this study, it is difficult to determine if micelles formed; however, the formation of smaller micelles and their adsorption below the normal micelle concentration might be a possibility. Whether or not surfactant micelles can be adsorbed at a solid-liquid interface is a debatable point. Certain data regarding adsorption of anionic surfactants indicate that adsorption maxima occur at or near the CMC (Harris, 1958, 1959). Others (Meader and Fries, 1952) show that surfactant adsorption displays adsorption maxima beyond the CMC. The latter observation would seem to support the assumption that micelles are adsorbed at a solid-liquid interface (clay-solution). Thus, in surfactant solutions containing ABS, anionic adsorption would probably dominate up to the CMC and then decrease; at this point, micelles would seem to control any adsorption phenomena. The formation of micelles would be favored in the presence of dissolved salt in solution—the maximum effect increasing with increase in charge in counter ion (cation) unless the cation became hydrolyzed.

When clay minerals are in acid solution containing aluminum salts, the effects of hydrolysis of Al^{+3} and subsequent complex formation may have a significant influence on ABS adsorption. The amphoteric nature of aluminum permits the consideration of specific ionic forms at different values of pH. According to Miller (1925), Al^{+3} predominates below pH 5 and $Al(OH)_4^{-1}$ forms in solutions above pH 7 from the dissolution of $Al(OH)_3$. In acid solution one possible hydrolysis scheme might be (Brosset and others, 1954):

$$6Al^{+3} + 15H_2O = Al_6(OH)_{15}^{+3} + 15H^{+1} \qquad (80)$$

Other possible complexes might be $Al(OH)^{+2}$, $Al_2(OH)_2^{+4}$, and $Al_3(OH)_6^{+3}$. Ruff and Tyree (1958) have also recognized the $Al_8(OH)_6^{+3}$ polymeric complex. If clay (kaolinite or montmorillonite) or soil are in solution with Al^{+3}, hydrolysis becomes more intense (Ragland and Coleman, 1960). It is unlikely that a source of Al^{+3} can be derived from gibbsite [$Al(OH)_3$] in natural materials because of its extreme stability (equilibrium solubility 1 to 3 months) and low solubility ($K_{SP} = 10^{-33.5}$ at 25°C) in water solutions or soil suspensions (Frink and Peech, 1962). The above data indicate that a variety of aluminum-hydroxy complexes might be formed and possibly adsorbed on clay surfaces. Adsorption of such complexes would increase the number of positive sites on clays. Hence, ABS could be attracted to these sites and be possibly adsorbed with the formation of a complex such as $Al_6(OH)_{15}^{+3}$ - $(ABS)_x$. Similar aluminum-hydroxy-ABS complexing has been suggested by Sedlander and Gates (1962). In alkaline solutions of aluminum salts, the aluminate ion, $Al(OH)_4^{-1}$, might compete with ABS for adsorption. The possibility of removing Al^{+3} from solution by precipitation of $Al(OH)_3$ and mechanically entrapping ABS was considered. No precipitation was observed in such solutions below pH 7. Unfortunately, data are not available for similar analogs of Ca^{+2} and Na^{+1}.

The decreased adsorption of ABS at high salt contents (2000 ppm) might be attributed to either precipitation of ABS micellar aggregates, if formed, or their inability to diffuse across the sausage membrane.

This portion of the study on clays has indicated that the removal of the surfactant (ABS) in detergents, which occurs in waste water, by natural clays is complex and inefficient as compared to removal by synthetic materials ("Baymal" and activated carbon). The adsorption capacity of clays for ABS increases with increase in concentration of ABS which obeys, in general, the Freundlich adsorption isotherm. Adsorption increases with increase in the number of carbon atoms in the alkyl chain for the types studied (C_{12} and C_{15}); apparently, the free energy of adsorption increases with increase in molecular weight. For all conditions studied, adsorption attains a maximum value at pH 4 as compared to either pH 7 or pH 10; the acid range no doubt creates significant numbers of positive sites on the clay surface, which are conducive to anionic ABS removal. When orthophosphate or carboxymethylcellulose are in solution with ABS, these anions do not interfere (compete) with ABS for adsorption sites. Some unknown mechanism(s) that aids in fixation of phosphate on clays seem(s) to enhance ABS removal when both are in solution. When ionized salts are in solution with ABS, the removal of ABS by clays is increased; this effect is most obvious in acid solution (pH 4) and increases as salt concentration increases to about 1000 ppm beyond which adsorption decreases with increase in salt concentration (between 1000 and 2000 ppm). ABS adsorption is generally favored for highly charged ionic salts; in some cases $Al^{+3} = Ca^{+2} > Na^{+1}$ and in others $Al^{+3} > Ca^{+2} > Na^{+1}$. Several complex physico-chemical phenomena must be considered to explain ABS adsorption in the presence of ionic salts.

Because most natural or sewage waste water has a pH of about 7, it seems obvious from this study that clay minerals in soils cannot adsorb significant amounts of ABS; this fact, therefore, alludes to a partial explanation of the pollution of ground water from ABS.

Studies on non-clay minerals.

In addition to adsorption of ABS on minerals, studies were made on the minerals glauconite, goethite, and gibbsite. These minerals are important because glauconite occurs as a dominant constituent of the so-called "Greensands" which are quite extensive in the Coastal Plain type of stratigraphy. Glauconite is also important because of its resemblance to illite and montmorillonite. Goethite and gibbsite are important in soils because these minerals may occur alone or as impurities in association with clay minerals, such as surface coatings or as mixtures, and may significantly influence adsorption of ABS.

Glauconite is loosely described as a hydrous, iron-alumina silicate and may be classified, generally, as a member of the illite clay group. Significant chemical entities have been listed by Burst (1958):

K_2O 7-8 per cent
Total Iron 20-25 per cent
Ferric: Ferrous 3-9 per cent.

Composition variations in glauconite have been reported as related to differences in mixed-layering involving "illite" (10 A°) and "montmorillonite" (expandable) layers (Hower, 1961). Other investigators (Levinson, 1955; and Yoder and Eugster, 1955) have suggested that the glauconite crystalline lattice resembles certain micaceous structures in a disorganized state. Selected analyses of glauconite from various localities are shown in table 20 (Burst, 1958) from which the calculated formulas of (1-3, table 20 respectively) are:

$K_{1.58}(Ca)_{0.10}(Al_{0.7}, Fe^{111}_{1.11}Fe^{11}_{0.49}Mg_{0.82})(Si_{7.22}Al_{0.78})O_{20}(OH)_4$

$K_{1.48}(Na_1Ca)_{0.51}(Al_{0.81}Fe^{111}_{1.97}Fe^{11}_{0.47}Mg_{0.66})(Si_{6.99}Al_{1.01})O_{20}(OH)_4$

$K_{1.20}(Na)_{0.09}(Al_{1.56}Fe^{111}_{1.47}Fe^{11}_{0.40}Mg_{0.62})(Si_{6.98}Al_{1.02})O_{20}(OH)_4$

where Fe^{111} = ferric
Fe^{11} = ferrous

Figure 58 shows the adsorption of dodecyl ABS on glauconite in terms of ABS concentration. Adsorption increases with increase in ABS concentration and obeys the Freundlich isotherm reasonable well (figure 51). Maximum adsorption takes place at pH 4 regardless of concentration; significant amounts of desorption occur only in concentrated solutions (100 ppm) for acid media. The amount of adsorption resembles closely that of illite, probably as a result of the similarity in structures.

Figure 59 shows the effect of orthophosphate on ABS (10 ppm) adsorption by glauconite. Maximum adsorption seems to occur in acid solution (pH 4) with little, if any, influence by phosphate. At pH 7, phosphate seems to interfere with adsorption of ABS for which no ready

Table 20.—Chemical analyses of glauconite from selected localities (Weight percent)

	1	2	3
SiO_2	47.1	48.0	47.5
Al_2O_3	11.5	10.7	15.5
Fe_2O_3	16.0	18.0	13.4
FeO	8.0	3.9	3.2
MgO	3.6	3.0	2.9
CaO	1.3	3.0	1.2
K_2O	8.2	7.8	6.4
Na_2O	.2	.2	..2
H_2O (100-1000°C)	6.4	7.4	11.1

1 - Franconia formation, Wisconsin
2 - Navesink formation, New Jersey
3 - Burditt formation, Texas

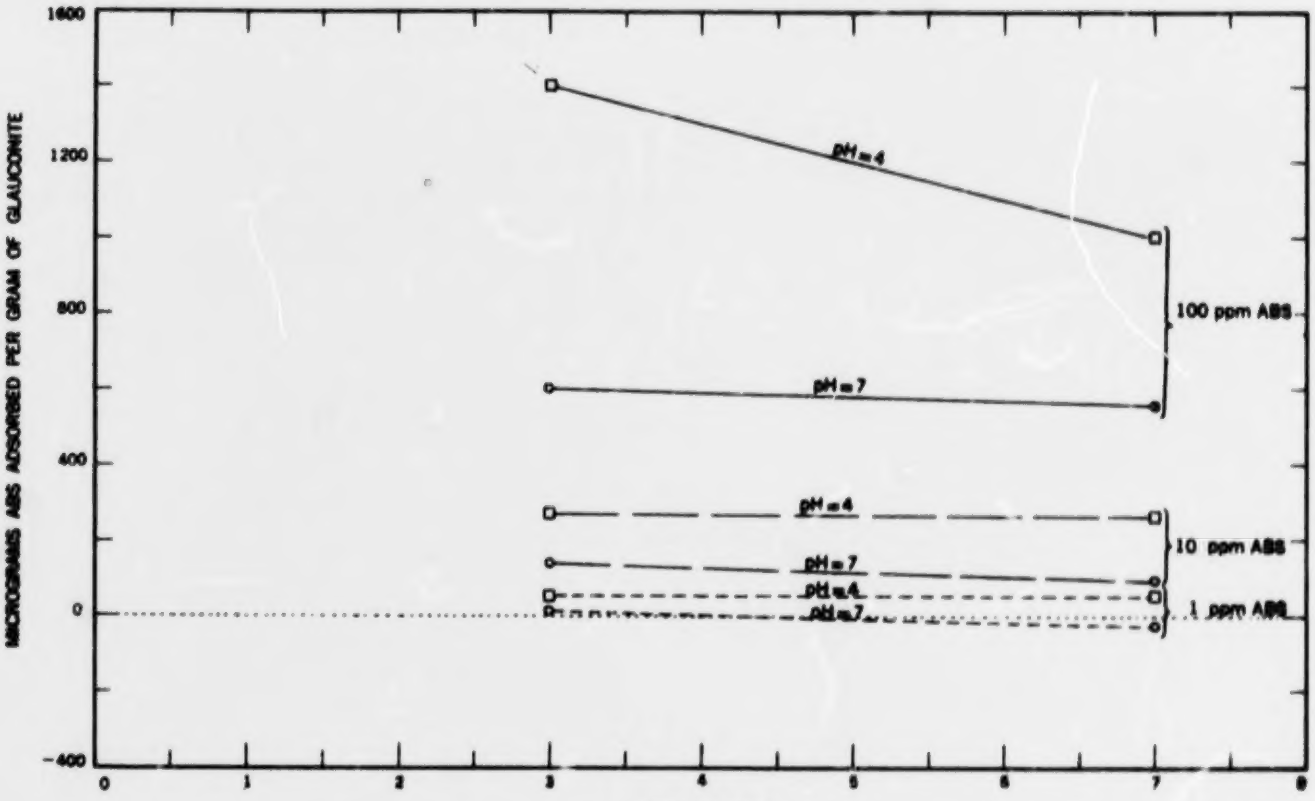


Figure 58.—Adsorption of dodecyl ABS on glauconite as a function of ABS concentration.

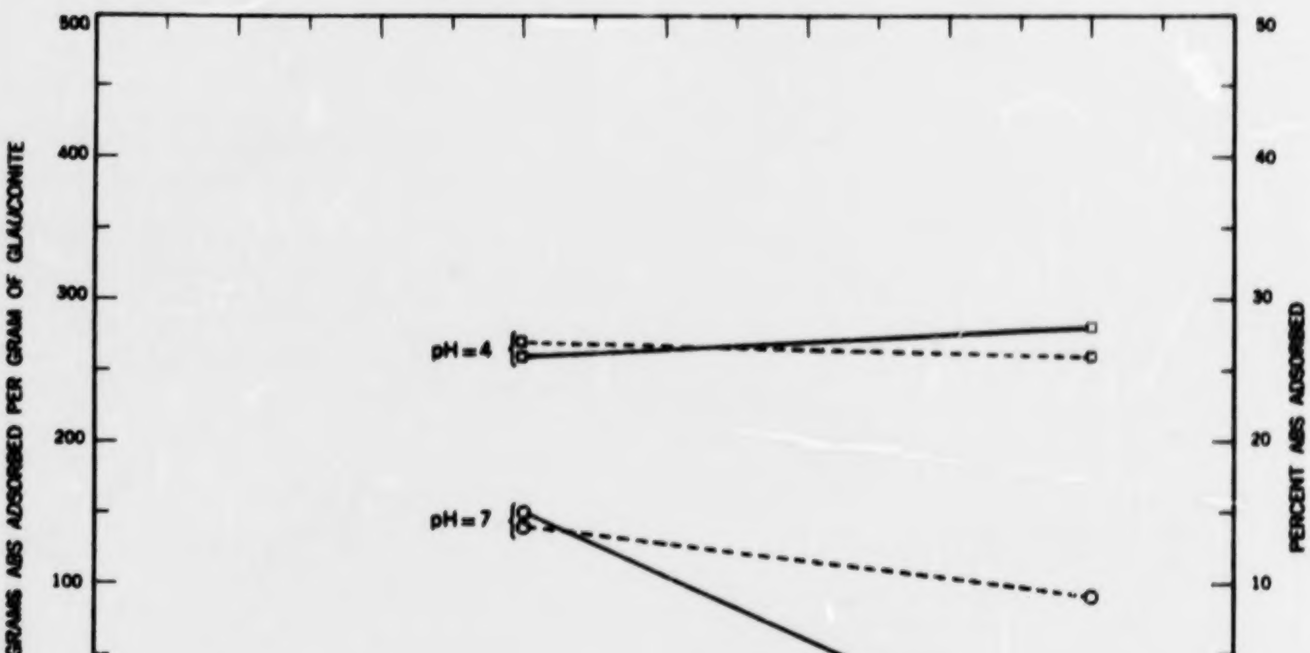


Figure 59.—Influence of orthophosphate on dodecyl ABS (10 ppm) adsorption by glauconite.

explanation is available, unless certain impurities in the glauconite cause ABS to precipitate in the presence of phosphate in neutral solutions.

Figures 60 to 62 show the amount of dodecyl ABS adsorbed by different amounts of NaCl, $CaCl_2$, and $AlCl_3$ at various pH respectively. The data show that optimum conditions for ABS removal are acid pH, high salt concentration, and highly charged ionized salts ($AlCl_3$). For solutions containing 1000 to 1500 ppm $AlCl_3$ (pH 4), over 80 percent of ABS can be adsorbed on glauconite. For the mono-and divalent salts, ABS adsorption values generally parallel those for the clay mineral illite. Because glauconite structure resembles that of a "degraded" illite, the properties of illite can be somewhat employed to account for the observations on glauconite; the similarity of these two minerals with regard to ABS adsorption is striking.

The amphoteric properties of both goethite [$Fe(OH)_3$] and gibbsite [$Al(OH)_3$] must be considered in interpreting its capacity to adsorb ABS. The charge on $Fe(OH)_3$ in solution has been described in terms of the solution pH (de Bruyn and Agar, 1962). The charge developed can be depicted as (positive surface)

$$Fe(OH)_3 + H^{+1} = Fe(OH)_2^{+1} + H_2O \qquad (81)$$

or as a negative surface by

$$Fe(OH)_3 = FeO_2^{-1} + H^+ + H_2O \qquad (82)$$

Thus (81) takes place by adsorption of H^{+1} to the solid, whereas, (82) occurs by the dissociation of a proton (addition of OH^{-1}). The pH at which the solid is neither negatively charged nor positively charged is called the zero point of charge (ZPC); this is the point at which the number of $Fe(OH)_2^{+1}$ and FeO_2^{-1} are equal and has been indicated as pH 8.5 (de Bruyn and Agar, 1962) and as pH 6.7 (Iwasaki and others, 1960). Dependent upon the most acceptable value of pH for ZPC, $Fe(OH)_3$ becomes positively or negatively charged below

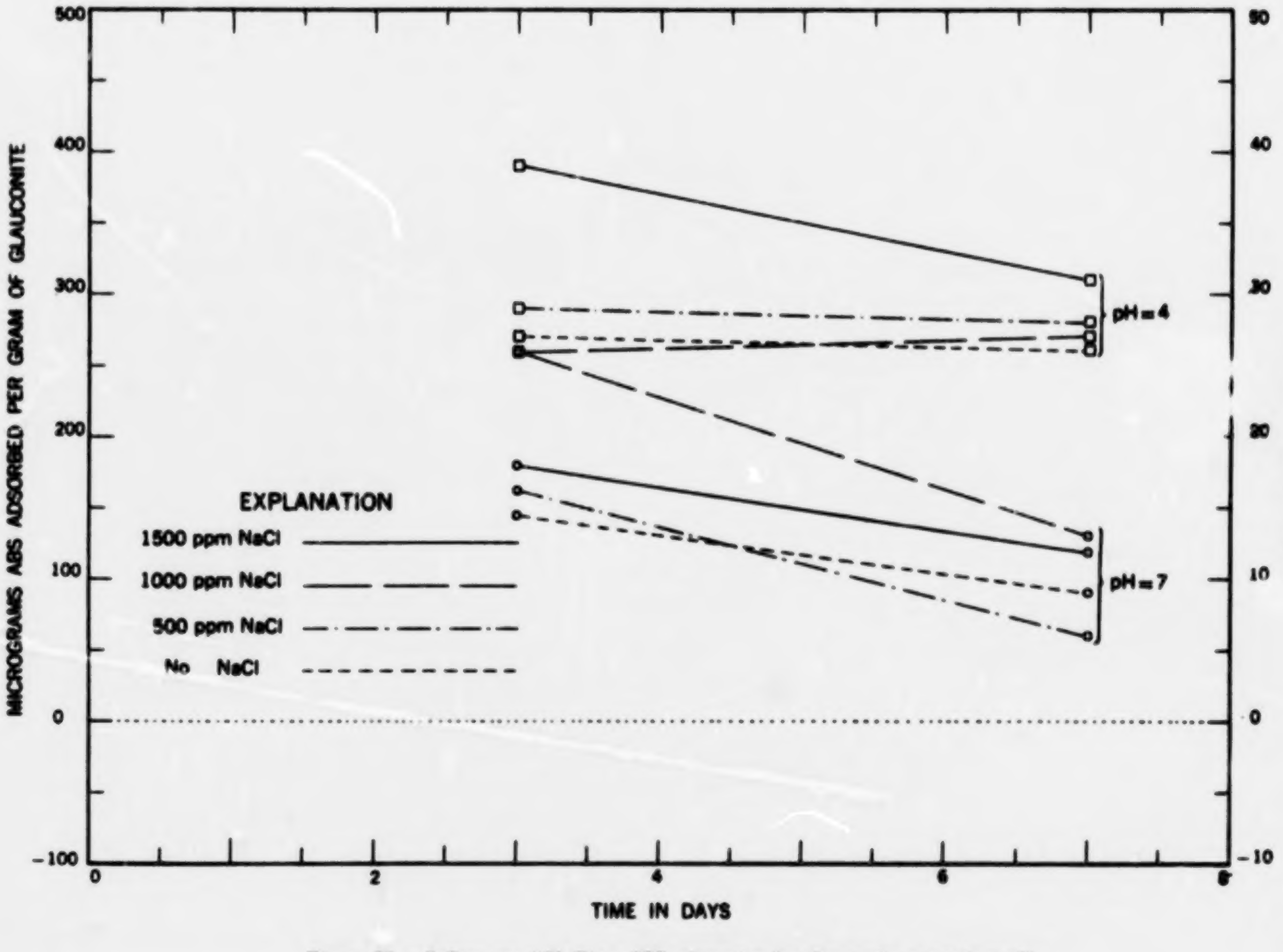


Figure 60. —Influence of NaCl on ABS adsorption by glauconite at various pH.

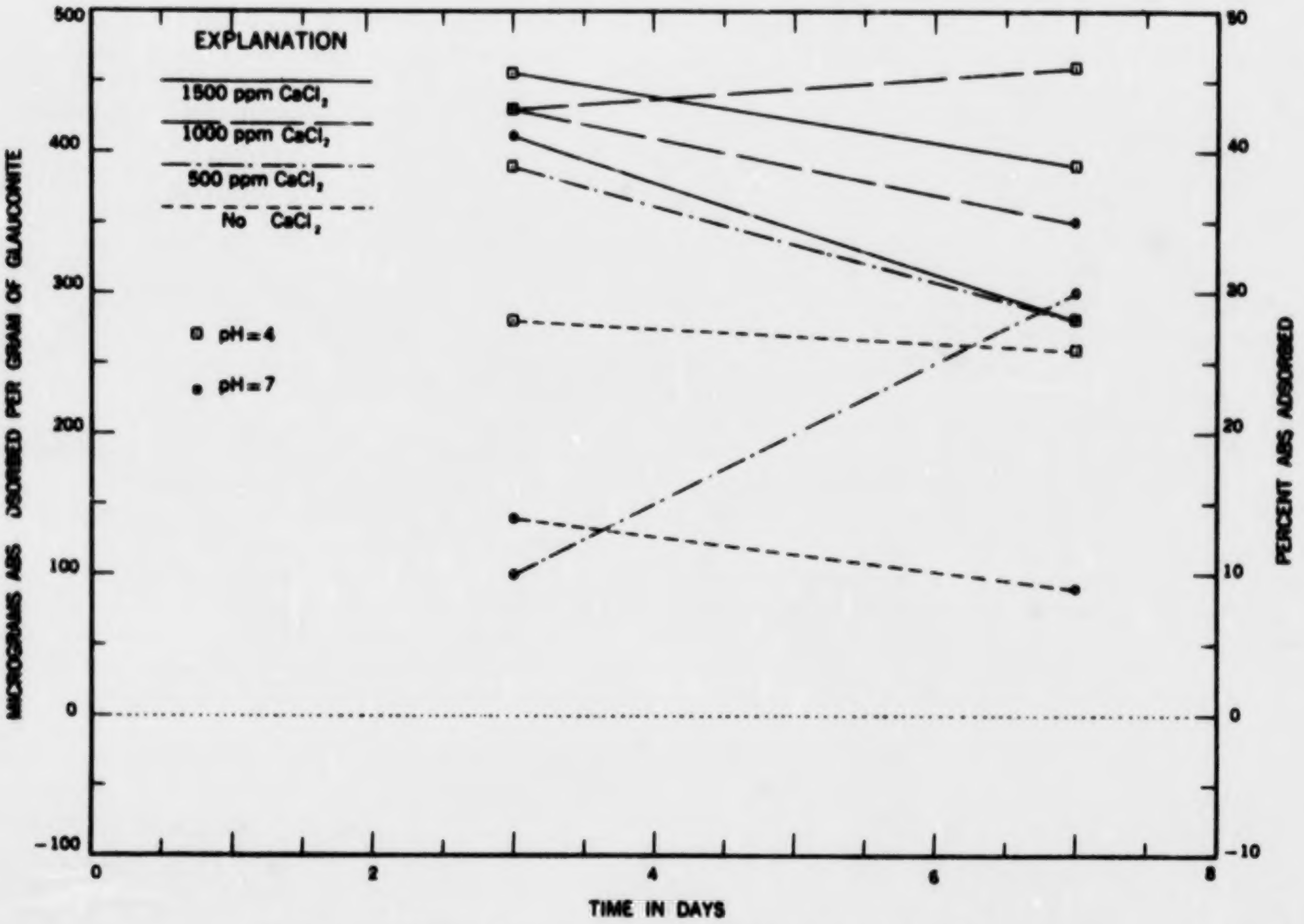


Figure 61.—Influence of $CaCl_2$ on ABS adsorption by glauconite at various pH.

and above this value, respectively. Thus, adsorption of ABS should proceed most readily at lower values of pH.

Figure 63 shows the adsorption of dodecyl ABS on goethite as a function of ABS concentration at various pH. The data indicate that adsorption of ABS increases with increase in concentration and obeys the Freundlich isotherm (figure 51). Maximum ABS adsorption seems to occur in acid solution (pH 4). A significant amount of adsorption-desorption phenomena takes place in concentrated ABS solutions (100 ppm).

Figure 64 shows the influence of orthophosphate (10 ppm) on adsorption of dodecyl ABS (10 ppm) by goethite. Phosphate seems to produce interference of ABS adsorption by adsorption-desorption phenomena. The maximum amount of ABS adsorption is in acid solution.

Figures 65 to 67 show the adsorption of dodecyl ABS (10 ppm) on goethite with different amounts of NaCl, $CaCl_2$, or $AlCl_3$ in solution at various pH. The effect of NaCl is maximum in acid solution but salt concentration is somewhat insignificant to adsorption (figure 65). $CaCl_2$ produces a greater amount of ABS adsorption than NaCl with its maximum effect in acid solution (pH 4) at 1500 ppm (figure 66). $AlCl_3$ exerts the greatest influence on ABS adsorption in acid solution (pH 4); in these solutions adsorption seems to decrease with increase in salt concentration between 500 and 1500 ppm but the amounts removed are significantly high ranging between 70 to 80 percent (figure 67).

The surface charge on gibbsite [$Al(OH)_3$] also depends on the solution pH and no doubt influences ABS adsorption as indicated for other minerals. In acid solution, Al^{+3} available on a gibbsite surface is subject to hydrolysis. The most probable complex to form in solution is (Brosset and others, 1954):

$$6Al^{+3} + 15H_2O = Al_6(OH)_{15}^{+3} + 15H^{+1} \qquad (83)$$

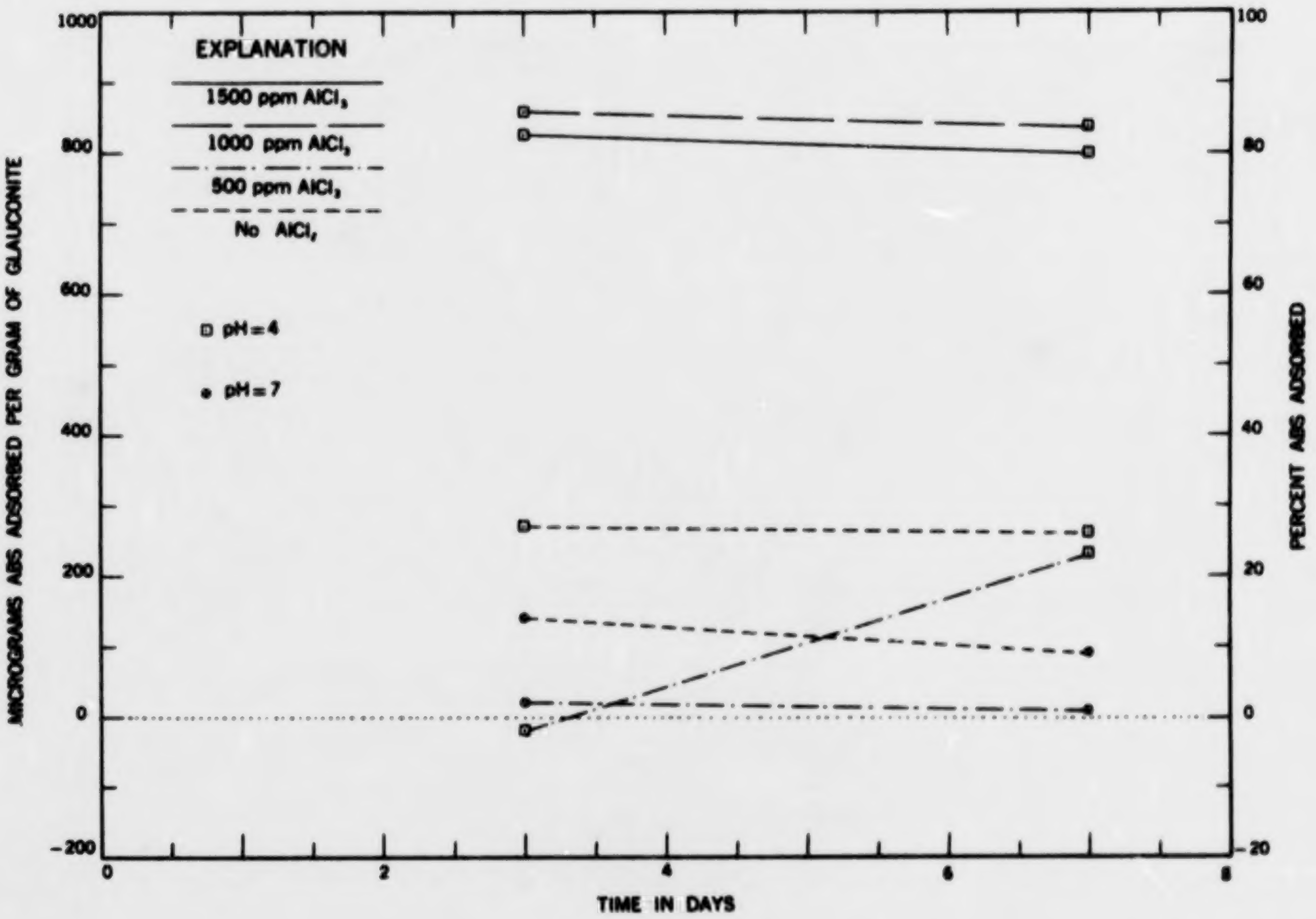


Figure 62.—Influence of $AlCl_3$ on ABS adsorption by glauconite at various pH.

but other possible complexes are $Al_2(OH)_2^{+4}$, $Al_3(OH)_6^{+3}$, $Al_6(OH)_{14}^{+4}$, and $Al_8(OH)_{20}^{+4}$. In alkaline solution as above the ZPC of goethite, gibbsite may acquire its surface charge from the reaction:

$$Al(OH)_3 + H_2O = Al(OH)_4^{-1} + H^{+1} \qquad (84)$$

The ZPC for gibbsite has been determined by electrokinetics as pH 5.0 (van Schuylenborgh and Säuger, 1949). Thus gibbsite should display positive and negative surface charge below and above pH of 5, respectively. Therefore, gibbsite should adsorb more ABS below pH 5 than above this value.

Figure 68 shows the influence of ABS concentration on its adsorption by gibbsite. The most obvious effect is that most ABS is adsorbed in acid solution (pH 4) as predicted from the ZPC. The amount of adsorption also increases with increase in ABS concentration as predicted from the Freundlich adsorption isotherm (figure 51). In the concentrated ABS solutions, severe desorption of ABS occurs with time of equilibration; this effect is probably, in part, a mechanical effect as a result of shaking the solutions during experimentation.

Figure 69 shows the influence of orthophosphate (10 ppm) on adsorption of ABS (10 ppm) by gibbsite. In those solutions (pH 4) where adsorption takes place readily, significant amounts of desorption are indicated. Regardless of pH, phosphate in solution seems to slightly depress ABS adsorption when both are in solution. This effect might be attributed to competition between ABS and phosphate for adsorption sites.

Figures 70 to 72 show the adsorption of dodecyl ABS (10 ppm) on gibbsite with different concentrations of NaCl, $CaCl_2$, or $AlCl_3$ in solution at various pH. NaCl seems to have little, if any, influence on ABS adsorption, especially at pH 4 (maximum adsorption);

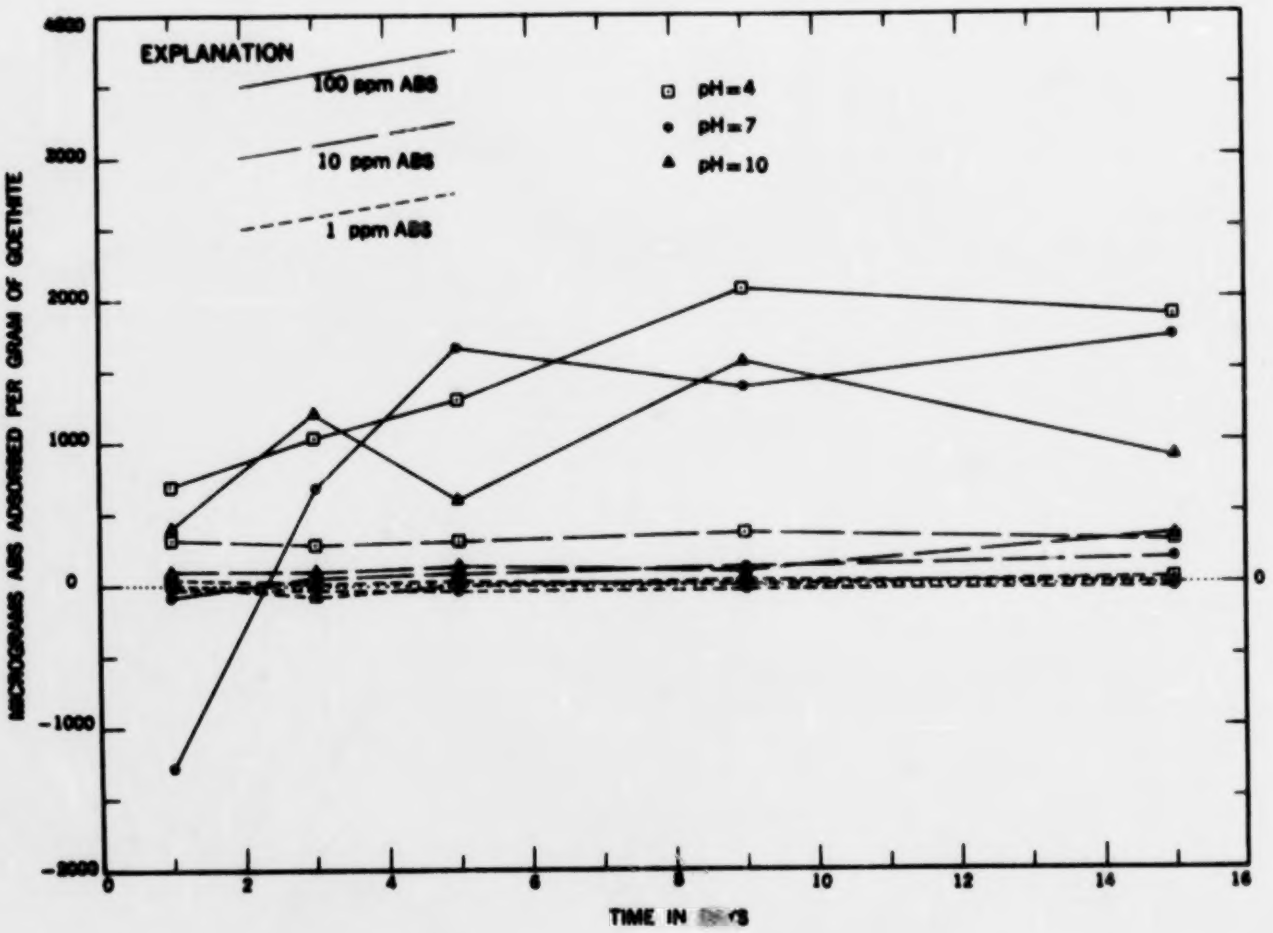


Figure 63. —Adsorption of dodecyl ABS on goethite as a function of ABS concentration at various pH.

low (500 ppm) and high (1500 ppm) amounts of salt seem to depress ABS adsorption slightly (figure 70). The effects of $CaCl_2$(figure 71) are quite similar to those for NaCl indicating little effect of charge difference between these salts on adsorption. $AlCl_3$ exerts a very signigicant effect on ABS adsorption, expecially at pH 4 and for solutions containing 1000 to 1500 ppm of $AlCl_3$; as equilibrium adsorption values are approached, over 80 percent of the ABS is removed from solution (figure 72).

Studies on Soils

Because the clay minerals and Fe-Al hydroxides comprise significant amounts of soils, adsorption of ABS on various soils was determined for comparative purposes. The physical characteristics and mineral constituents of the various soils are given in the subsequent section on column studies.

Figures 73 to 79 show the adsorption from solutions containing 5 ppm of dodecyl ABS and different amounts of NaCl and $CaCl_2$ at various pH. The data show that adsorption values for optimum conditions (high concentrations of $CaCl_2$ in solution) range from about 200 μg/g (Muck soil). Solutions containing only ABS also reveal that acid solutions (pH 4) produce maximum amounts of adsorption on these soils. The data in general can be correlated with adsorption values obtained for the clay minerals, Fe-Al hydroxides, and glauconite; the importance of these compounds to removal of ABS from solution is significant. The lowest and highest adsorption values for the soils are probably attributed to the high contents of quartz (Adobe and Loess soils) and organic material (Muck), respectively.

Figure 80 shows the influence of organic matter in soils on adsorption from solutions containing 5 ppm ABS, 1000 ppm $CaCl_2$ at pH 7. It is apparent that amount of organic matter in soil has a marked influence on ABS adsorption. This effect is difficult to explain but might arise from the amphoteric nature of organic matter in soils and the

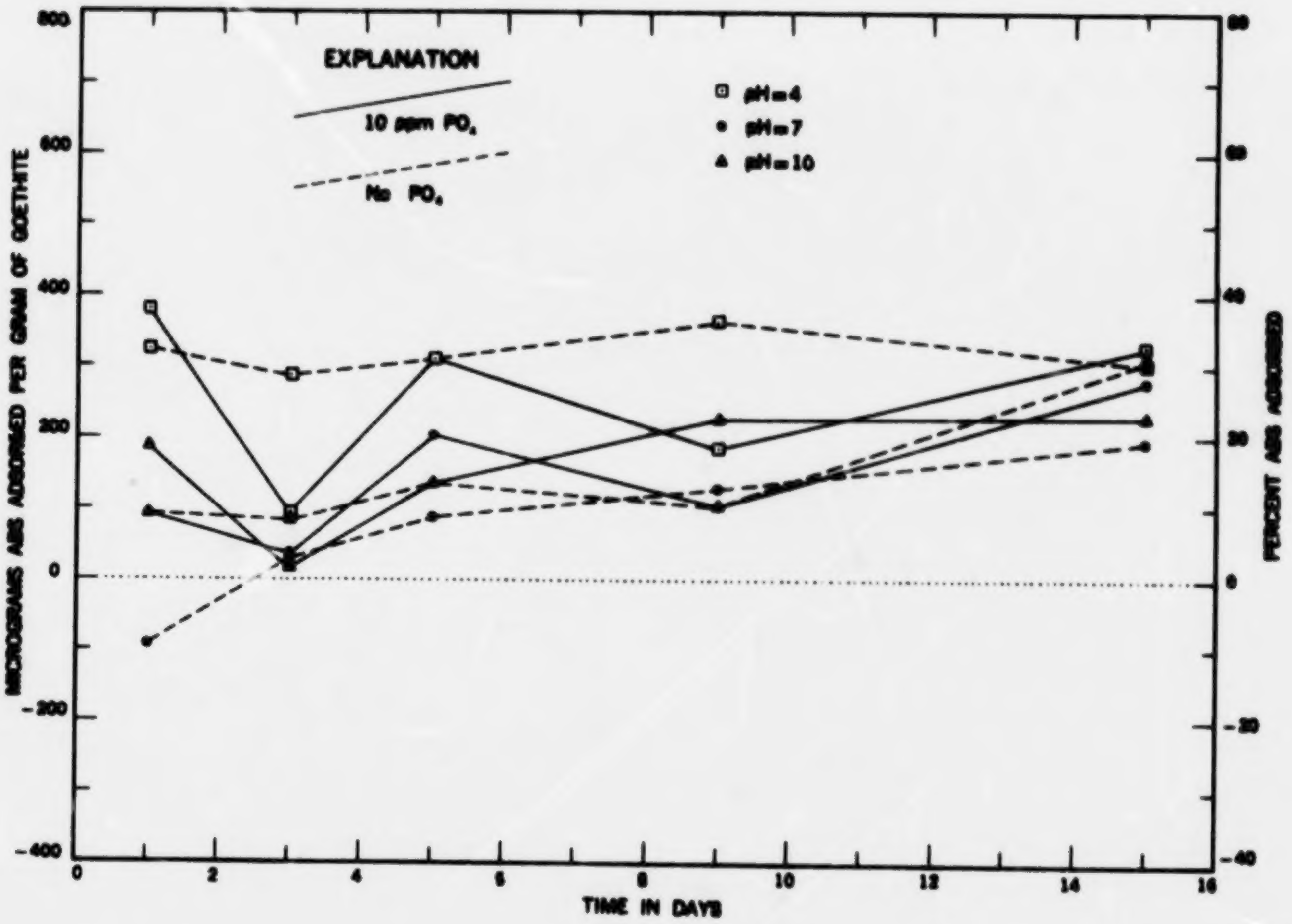


Figure 64. —Influence of orthophosphate on dodecyl ABS adsorption by goethite.

development of positive charges on such material. Similar observations have been made by Chao (1960) on the adsorption of sulfate by soils containing high contents of organic matter.

Figure 81 shows adsorption of decyl ABS (5 ppm) at pH 7 on various Long Island aquifer sands. These sands contained about 95 percent quartz with the remaining 5 percent containing muscovite, hornblende, feldspar, iron oxide, and rock fragments. Most quartz grains contained various amounts of iron stain coatings that increased in the order of curves 1, 2, 3a. Curve 3b was leached with concentrated nitric acid. Quartz is normally charged negatively in natural water. The ZPC of quartz has been indicated at pH 2 (Iwasaki and others, 1961), pH 3.0 (Li, 1958), and pH 3.7 (Gaudin and Fuerstenau, 1955). Thus, depending on the previous history of the quartz, which determines the ZPC, its charge in solutions probably above pH 3.5 is negative. This characteristic, along with its insignificant amount of surface area, prevent significant amounts of ABS to be adsorbed from solution. Most studies on quartz sand show that the amount of ABS removed from solution ranged from about 3 to 20 µg/g (figure 7). The amount removed depends somewhat on the surface area (Wayman, 1962b) and bacterial coatings (growth), (Ewing and others, 1962) on these grains. Studies on the Long Island aquifer sands show that ABS removed attained equilibrium values that ranged from about 50 to 100 µg ABS/g sand (curves 1, 3a). These values no doubt are influenced by iron oxide (hydroxide) coatings on these grains. The leached sand showed that the amount of ABS removed, in absence of the coating, was about zero (curve 3b).

This portion of the study has shown that most natural materials display an inefficient tendency to remove ABS from solution. This effect supports much of the data in the literature for pollution of ground water from ABS. Certain of the natural materials such as

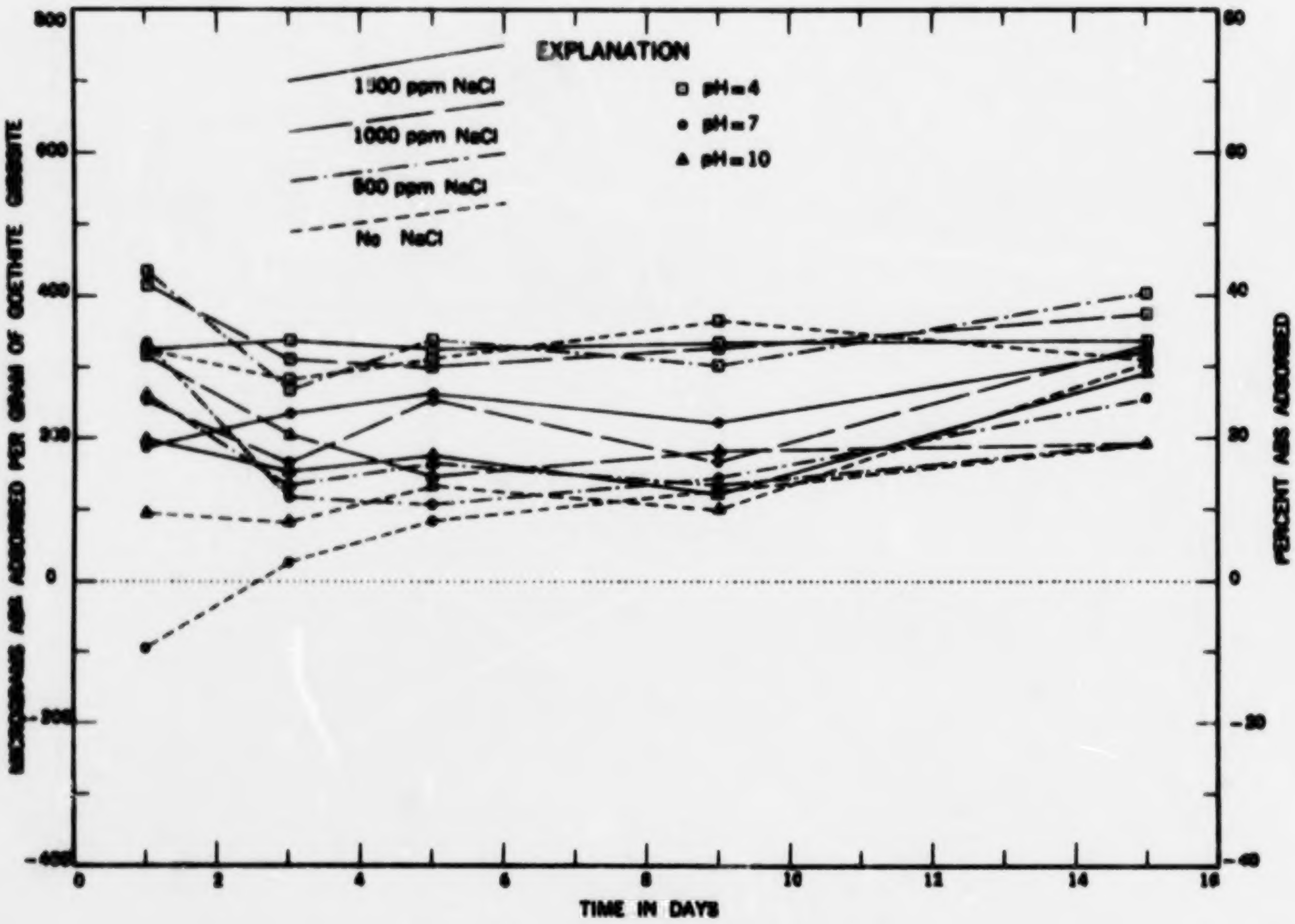


Figure 65.—Influence of NaCl on dodecyl ABS adsorption by goethite at various pH.

goethite or gibbsite seem to possess the best adsorptive properties for ABS and may serve as filter aids in pollution studies.

The adsorption capacities of soils for ABS closely approximate the values obtained for the various natural materials studied except quartz sands. The gross interpretation of the results is best explained in terms of the charge development on the surface of solids and the ionic charge on the solute. The ability of natural materials to remove ABS is complex and depends upon:

(1) concentration of ABS in solution

(2) length of the alkyl chain (number of carbon atoms)

(3) pH of the solution

(4) in some instances having phosphate in solution, especially for clays

(5) type and amount of ionized salt in solution

(6) amount of organic matter.

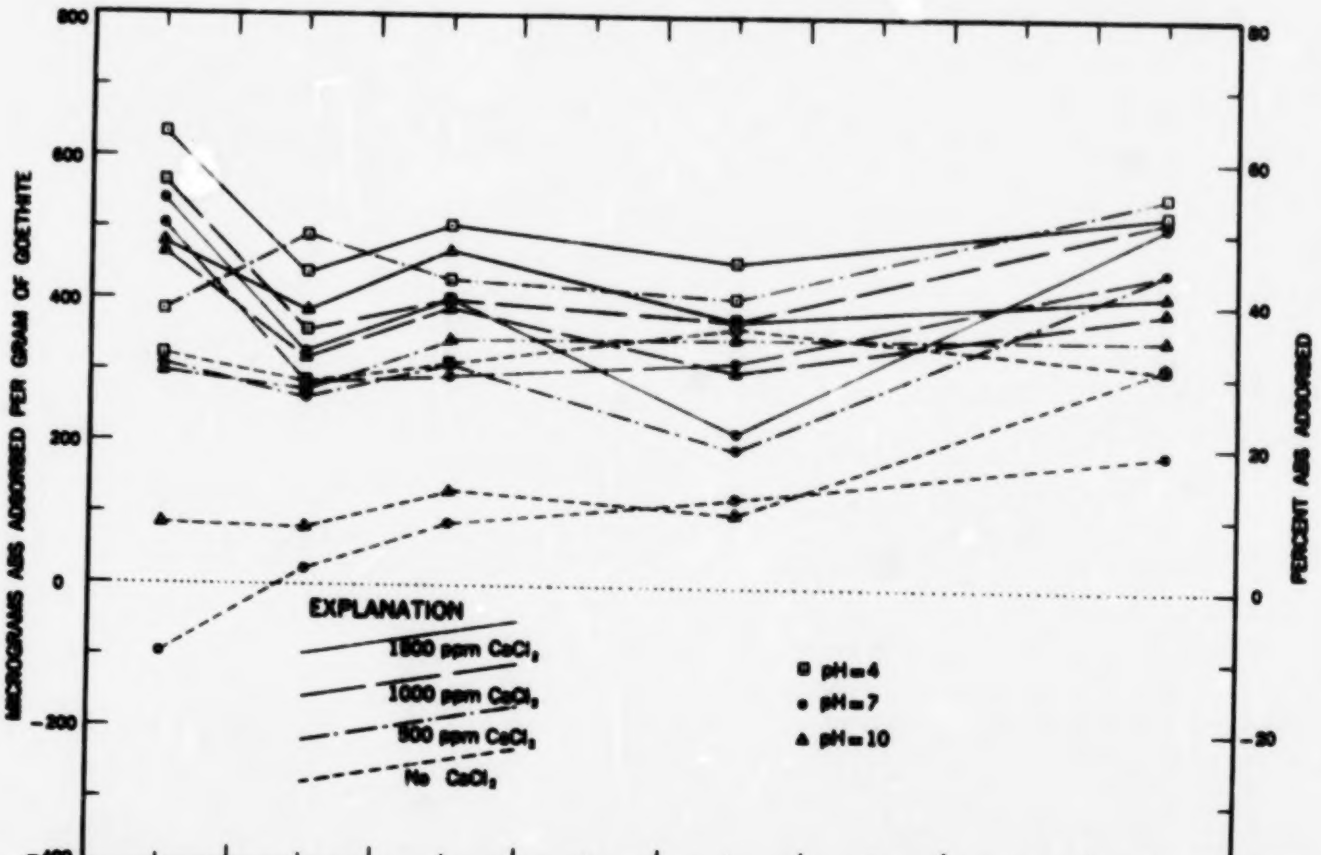


Figure 66.—Influence of $CaCl_2$ on dodecyl ABS adsorption by goethite at various pH.

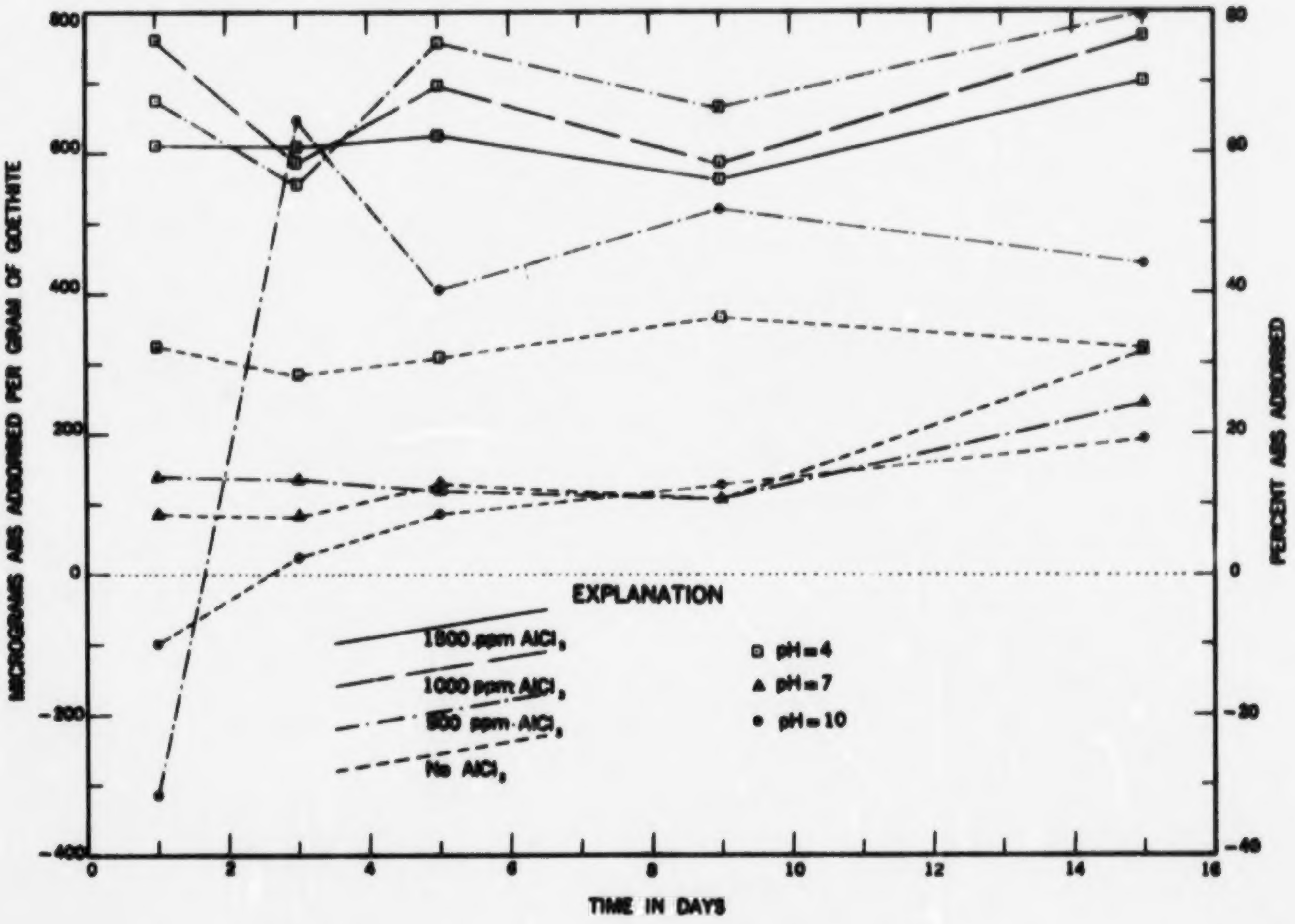


Figure 67.—Influence of AlCl$_3$ on dodecyl ABS adsorption by goethite at various pH.

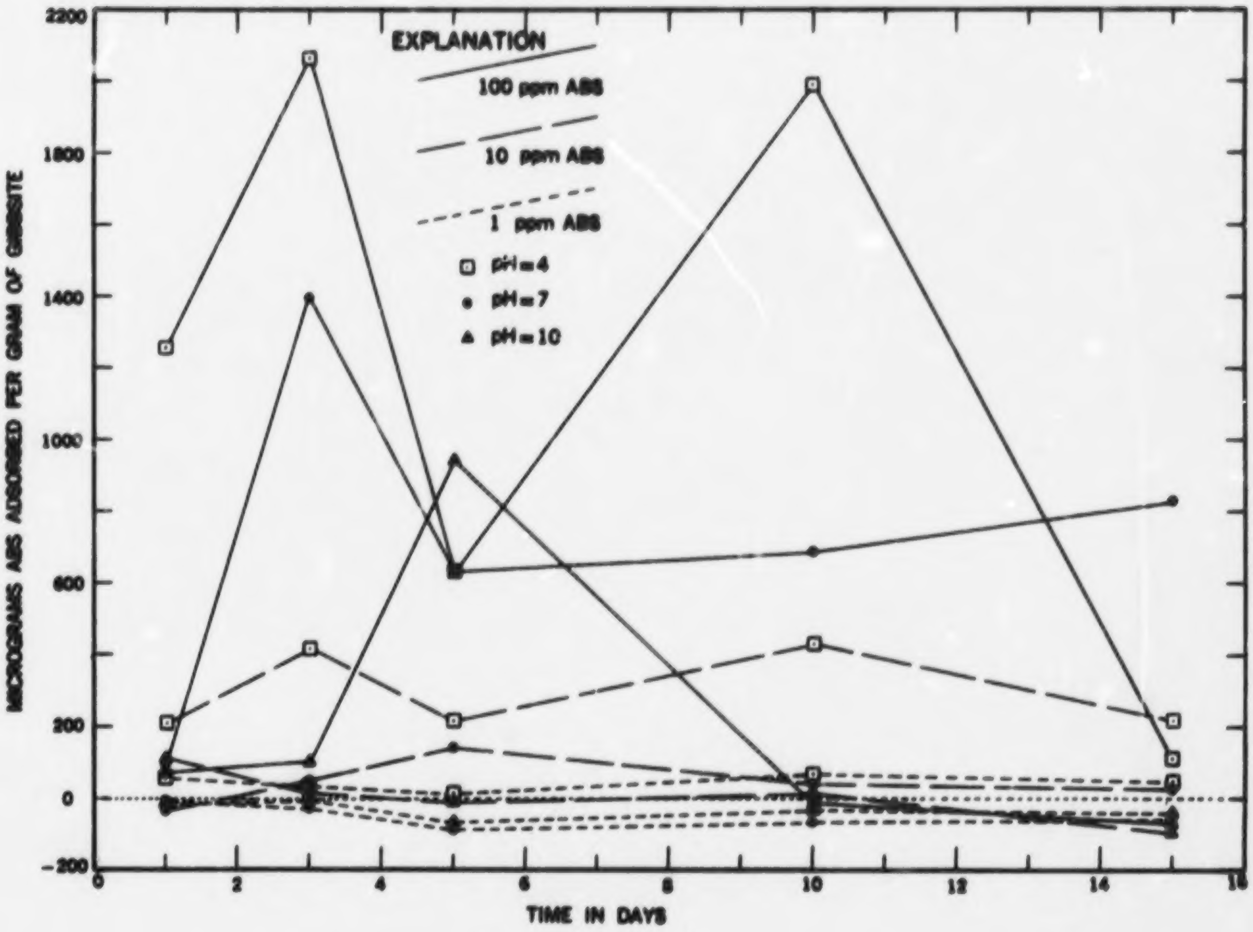


Figure 68.—Influence of dodecyl ABS concentration on its adsorption by gibbsite.

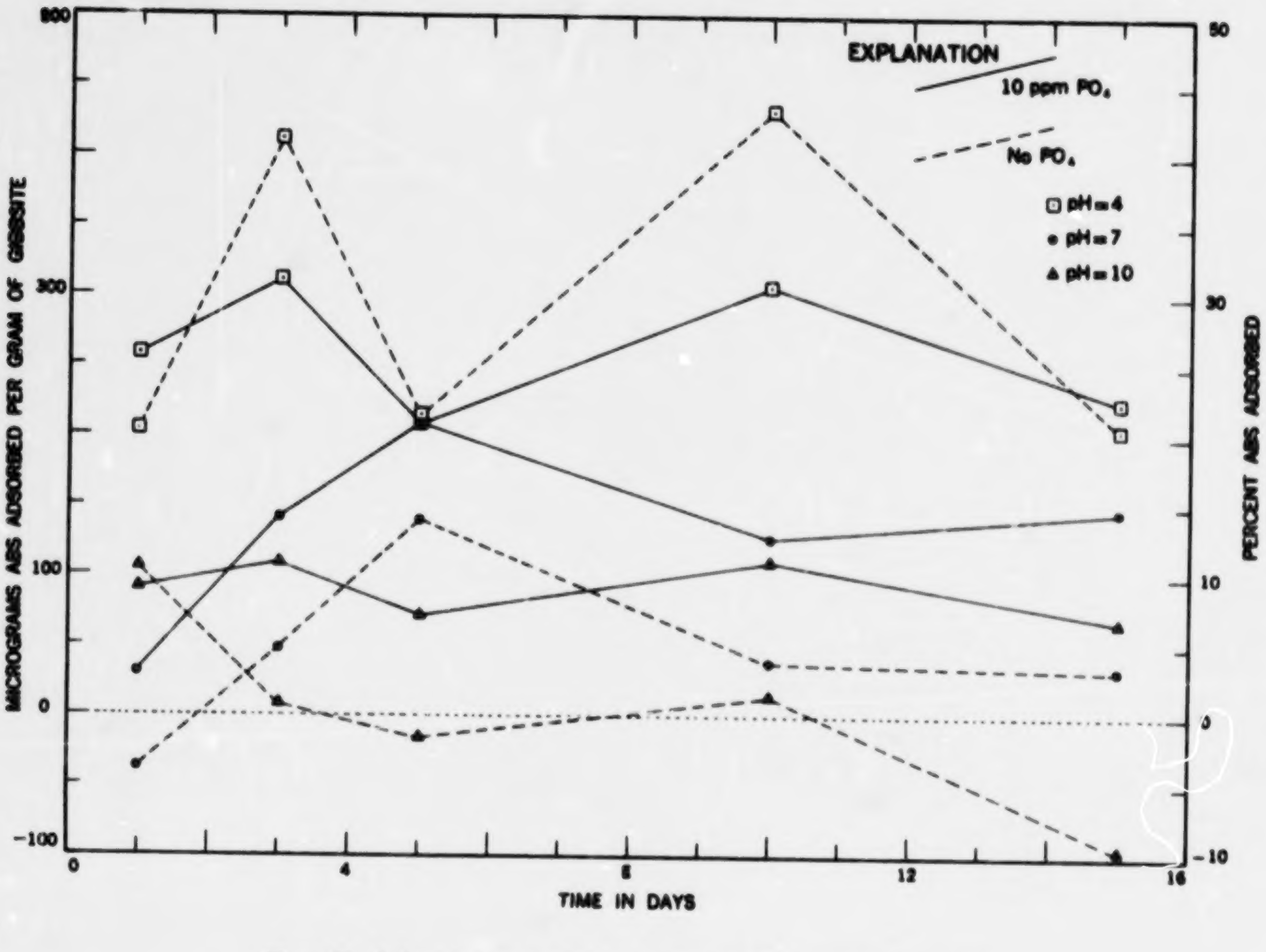


Figure 69.—Influence of orthophosphate on dodecyl ABS adsorption by gibbsite.

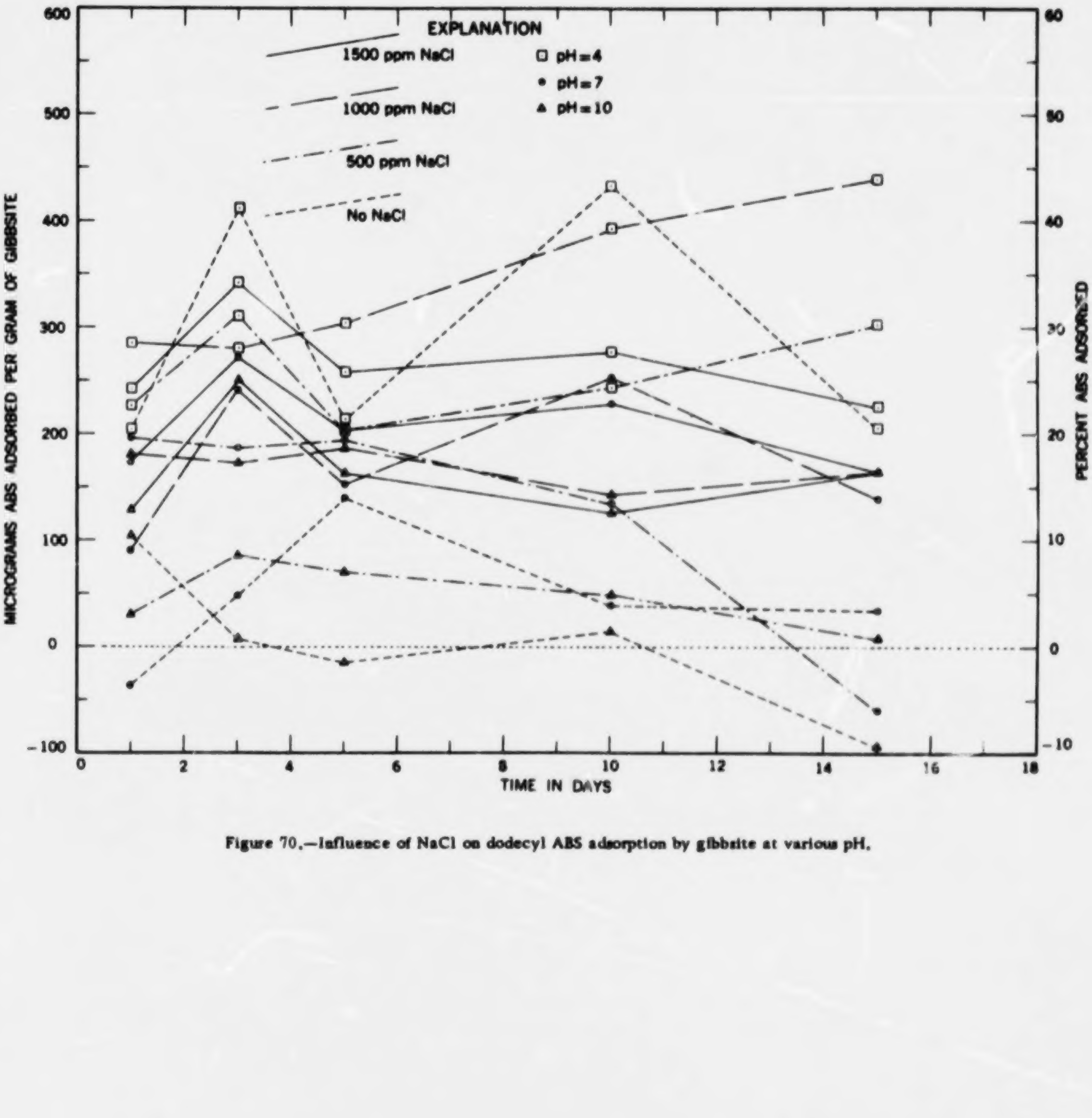


Figure 70.—Influence of NaCl on dodecyl ABS adsorption by gibbsite at various pH.

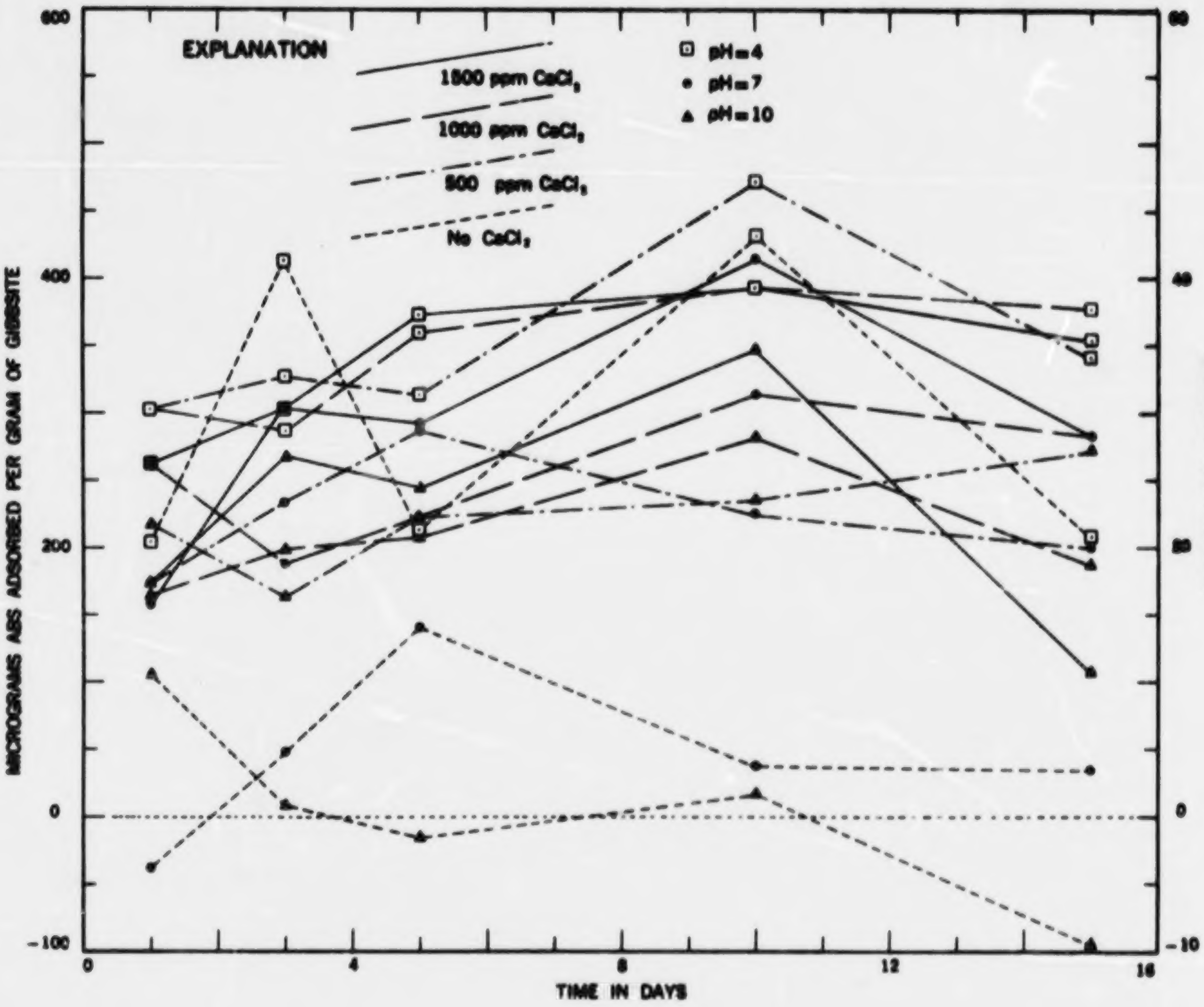


Figure 71.—Influence of $CaCl_2$ on dodecyl ABS adsorption by gibbsite at various pH.

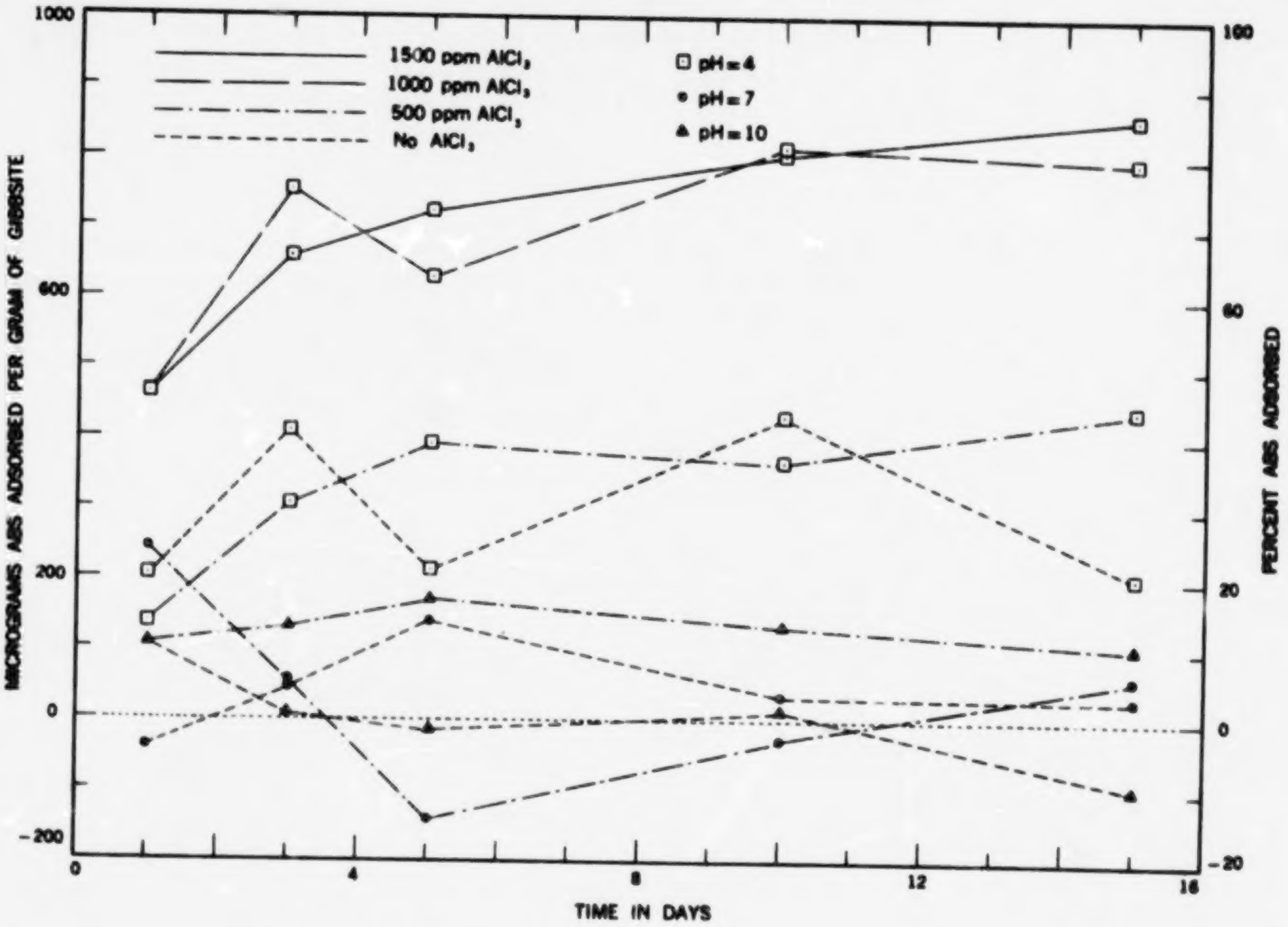


Figure 72.—Influence of $AlCl_3$ on dodecyl ABS adsorption by gibbsite at various pH.

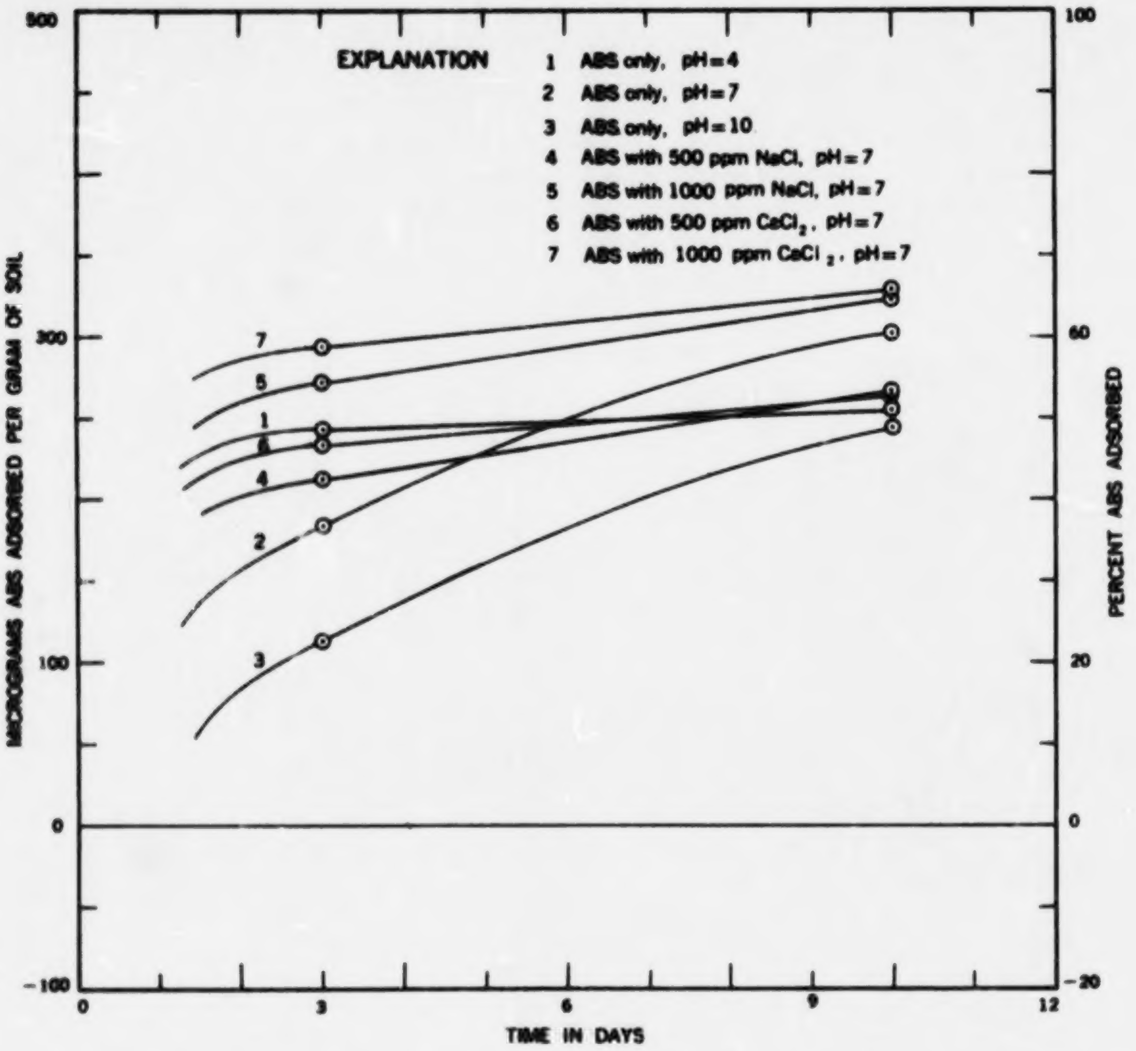


Figure 73.—Adsorption of dodecyl ABS from a solution at 25 degrees Centigrade, containing 5 ppm dodecyl ABS, on 200 mg of greensand marl soil.

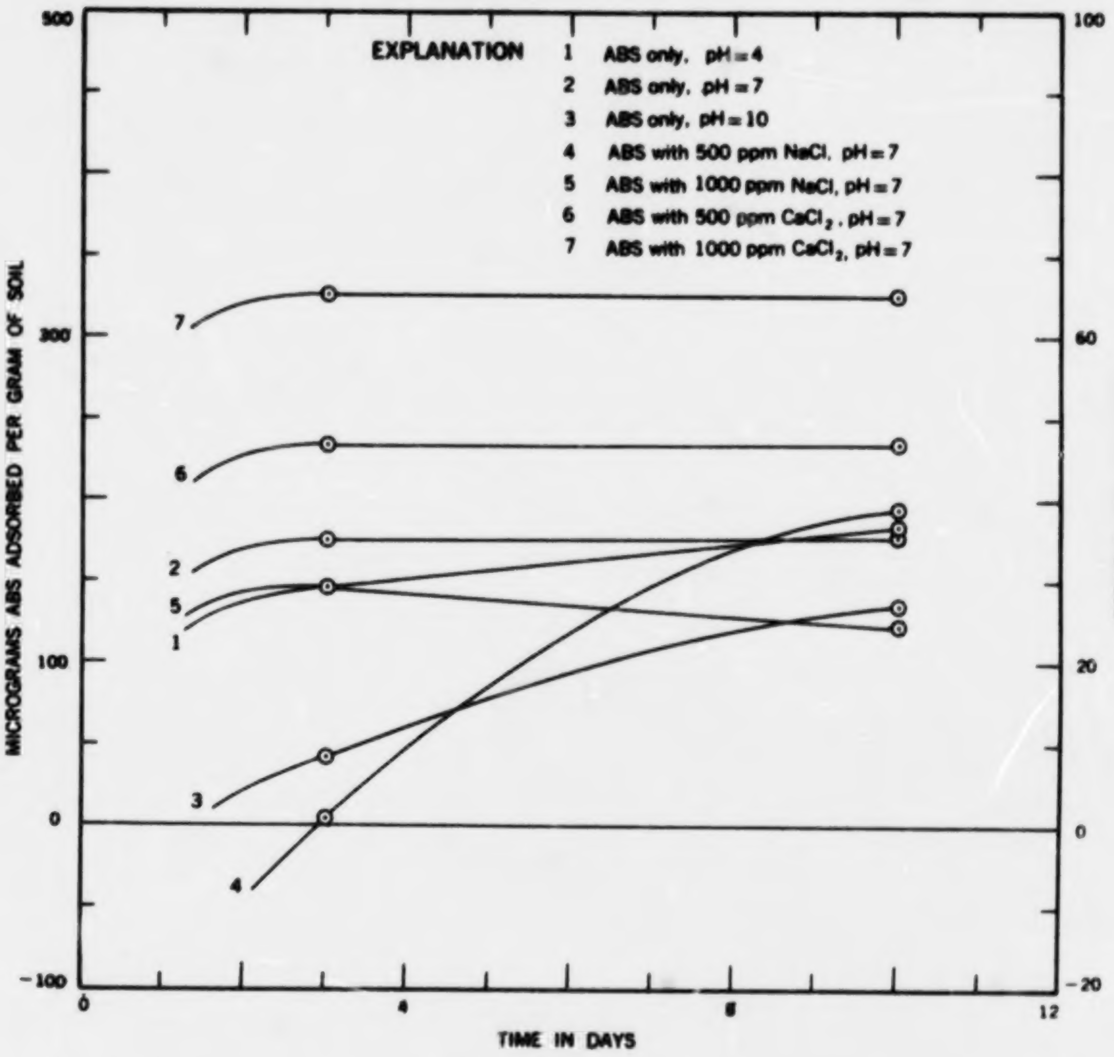


Figure 74.—Adsorption of dodecyl ABS from a solution at 25 degrees Centigrade, containing 5 ppm dodecyl ABS, on 200 mg of weathered basalt soil.

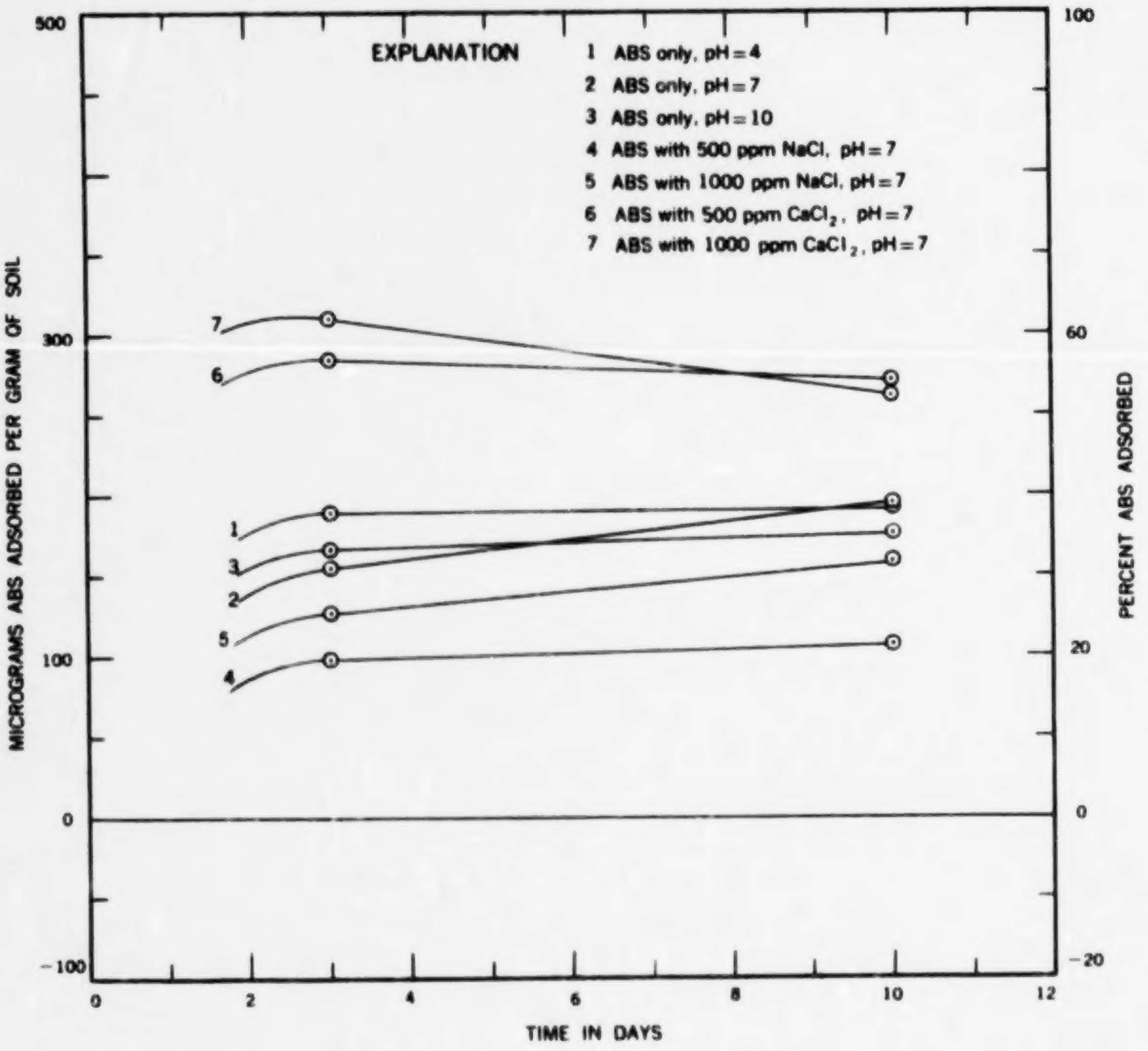


Figure 75.—Adsorption of dodecyl ABS from a solution at 25 degrees Centigrade, containing 5 ppm dodecyl ABS, on 200 mg of sandy-loam soil (Brighton, Colorado).

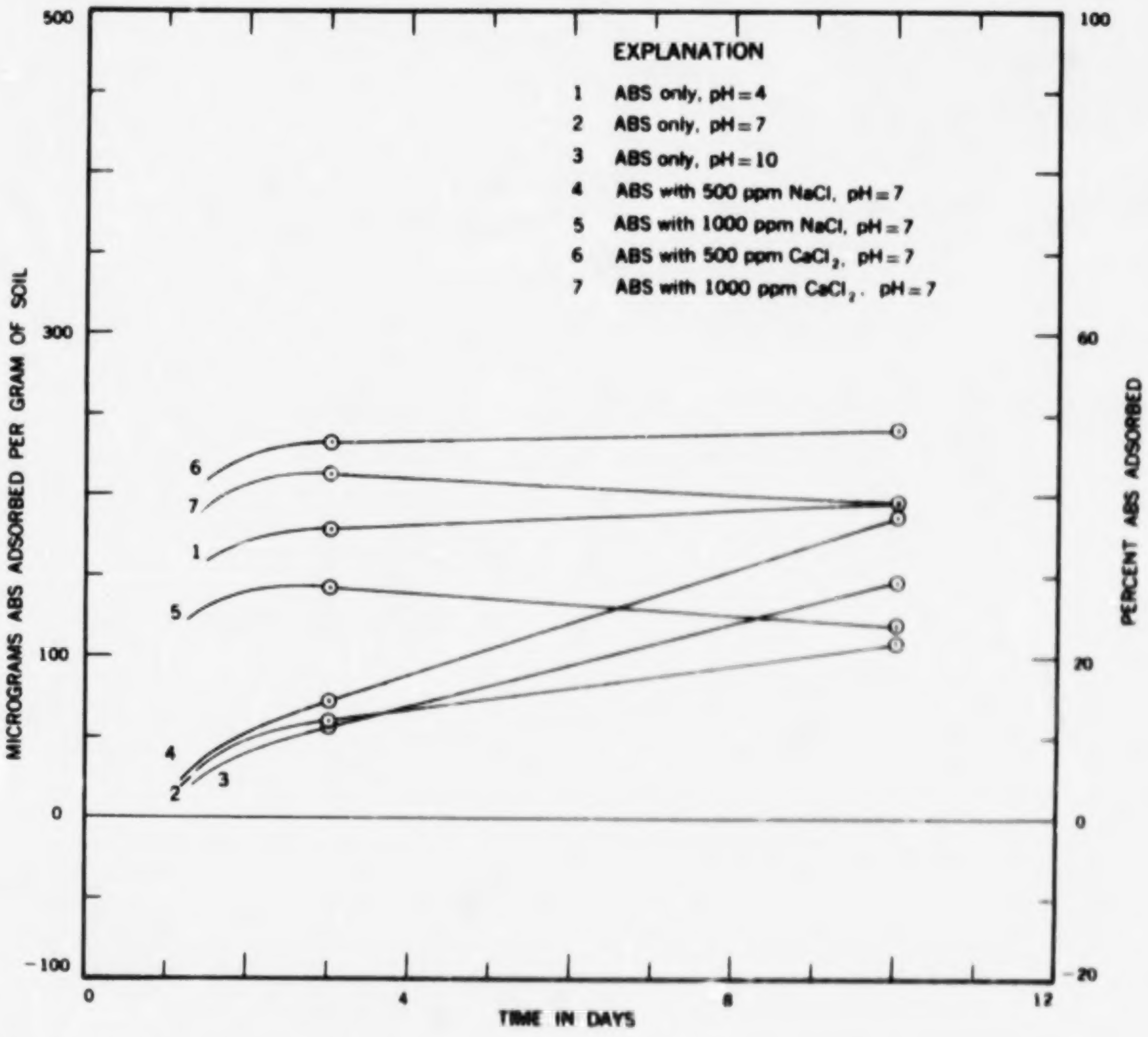


Figure 76.—Adsorption of dodecyl ABS from a solution at 25 degrees Centigrade, containing 5 ppm dodecyl ABS, on 200 mg of weathered hornblende-schist soil.

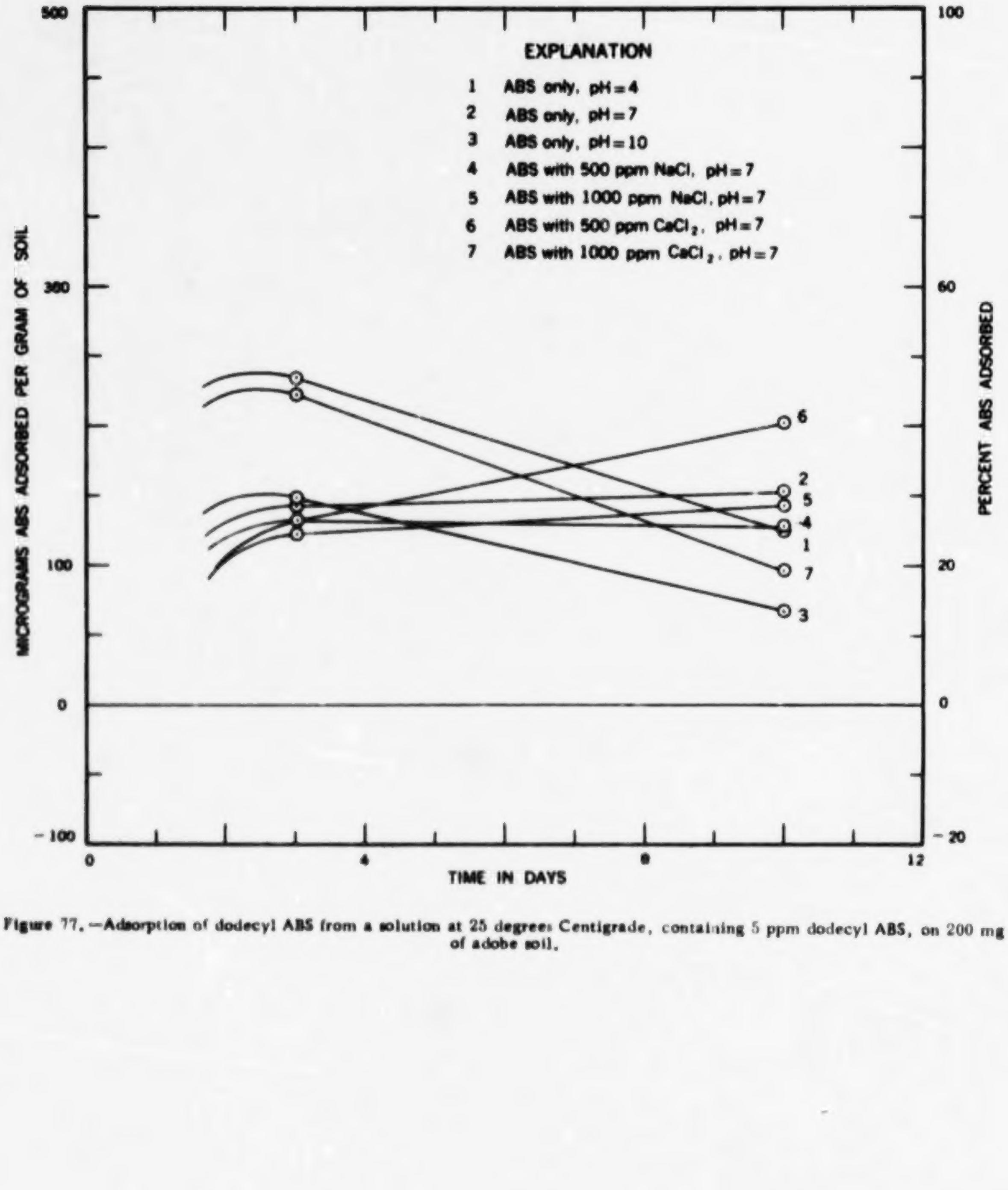


Figure 77. —Adsorption of dodecyl ABS from a solution at 25 degrees Centigrade, containing 5 ppm dodecyl ABS, on 200 mg of adobe soil.

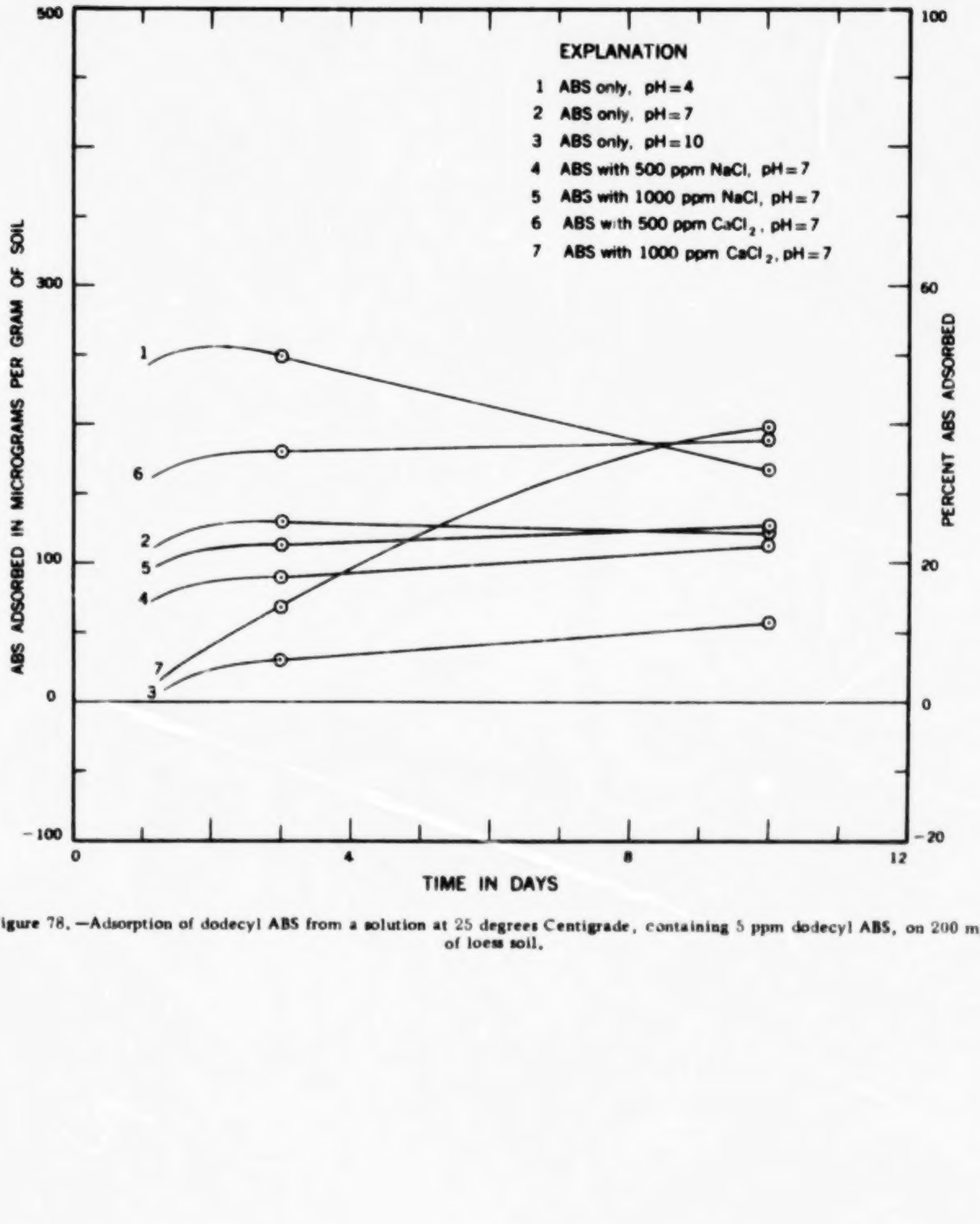


Figure 78.—Adsorption of dodecyl ABS from a solution at 25 degrees Centigrade, containing 5 ppm dodecyl ABS, on 200 mg of loess soil.

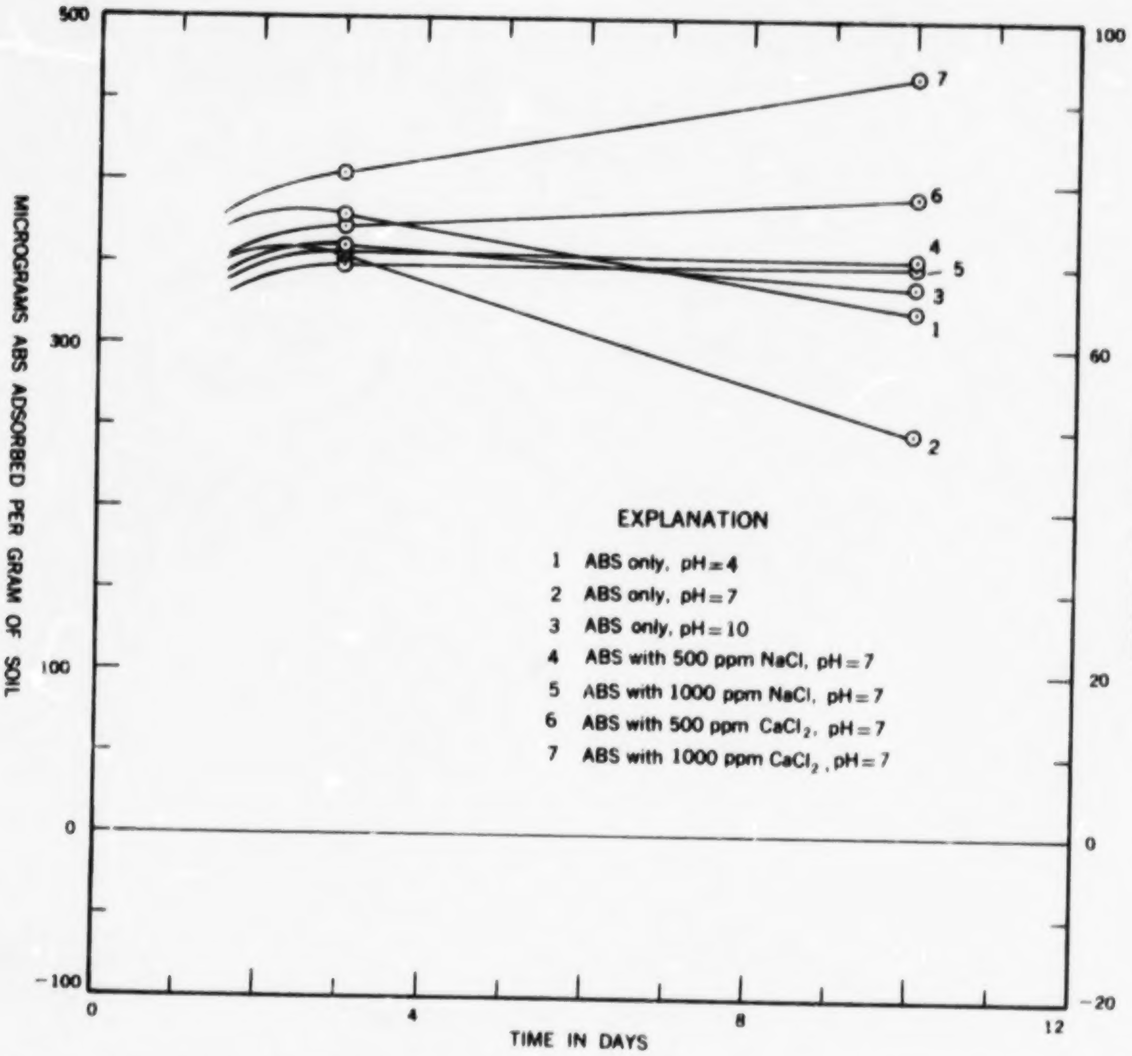


Figure 79.—Adsorption of dodecyl ABS from a solution at 25 degrees Centigrade, containing 5 ppm dodecyl ABS, on 200 mg of muck soil.

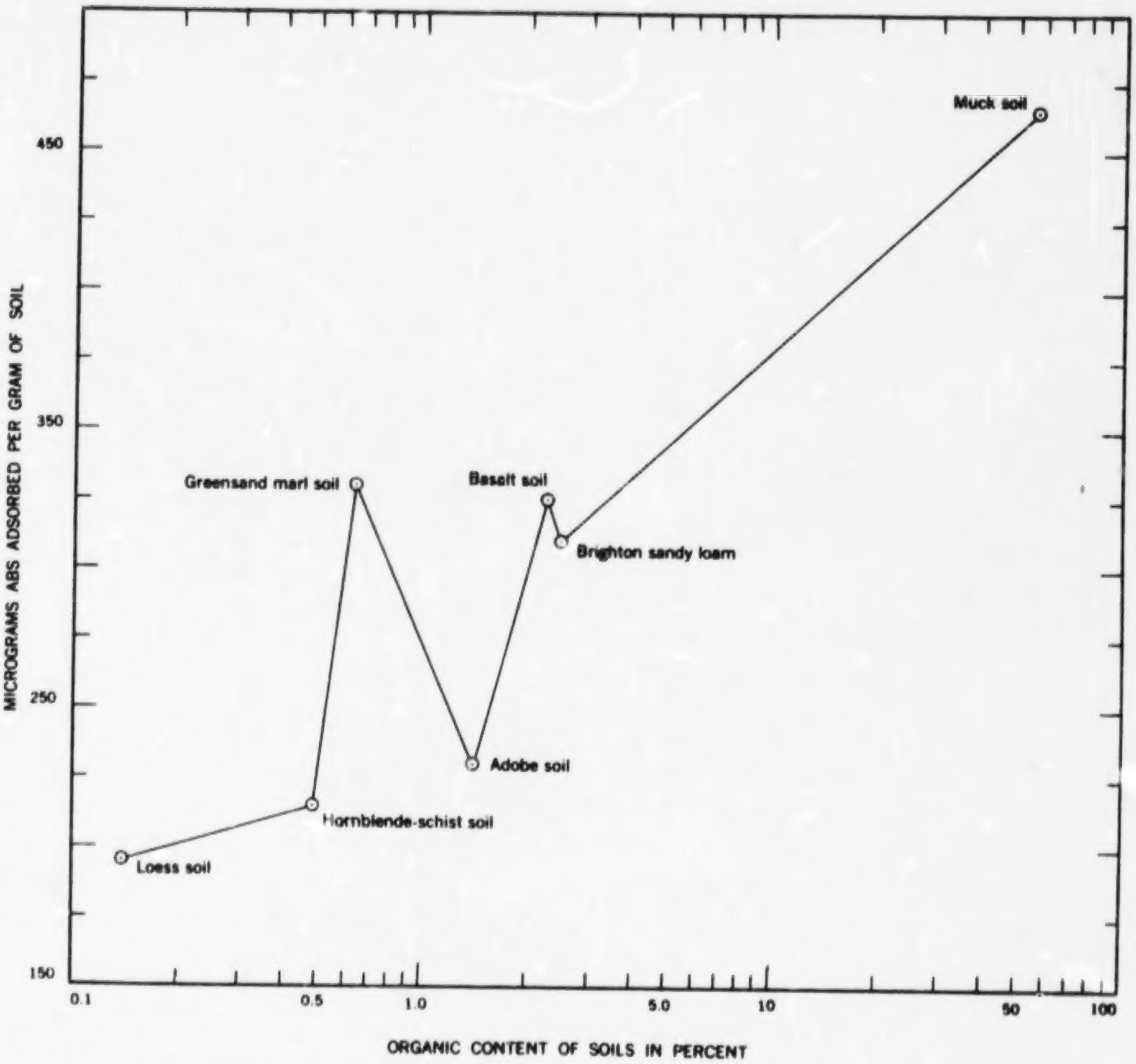


Figure 80. —Adsorption of dodecyl ABS from a solution at 25 degrees Centigrade, containing 5 ppm dodecyl ABS and 1000 ppm of calcium chloride, as a function of organic content of soil.

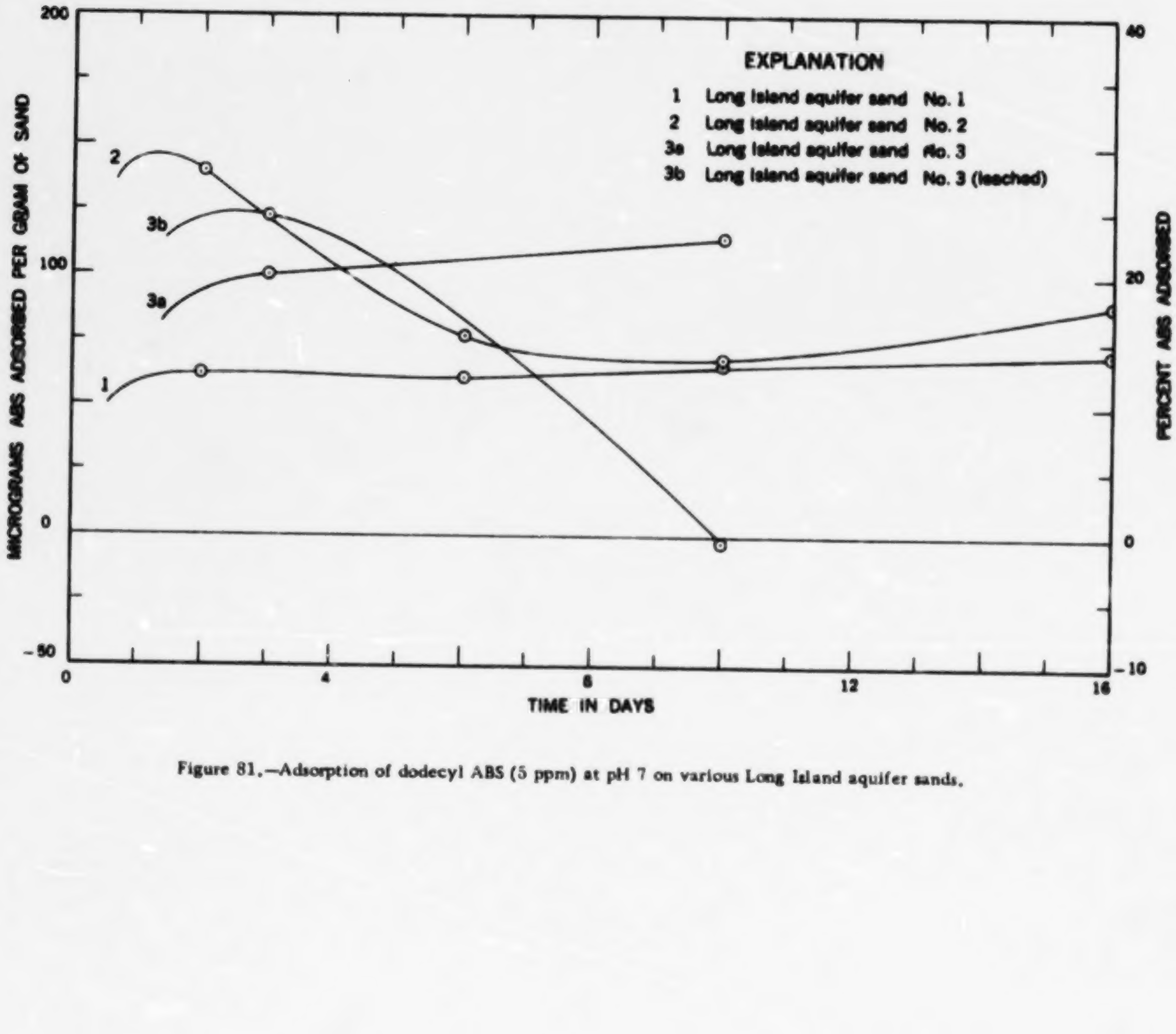


Figure 81.—Adsorption of dodecyl ABS (5 ppm) at pH 7 on various Long Island aquifer sands.

BEHAVIOR OF SURFACTANTS AND OTHER CONSTITUENTS IN TREATED SEWAGE IN WATER-SATURATED SOIL COLUMNS

In the previous section adsorption characteristics of ABS on various natural materials were described. This section contains data relating the removal of ABS, dissolved solids, bacteria, and changes in pH to infiltration of a typical waste-water solution (Denver Treatment Plant Primary Effluent) through various types of soils in the United States. Such studies allude to the manner in which ABS and other constituents discharged as natural waste solutions behave in soils which become water-saturated as in natural ground water aquifers.

Previous studies on the infiltration of waste-water or solutions containing ABS and other constituents through soil columns are limited. Robeck and others (1962-a) showed that the ABS content does not significantly influence the rate of growth of coliform bacteria (Escherichia coli) or their movement through water-saturated sands. In a study on unsaturated flow, Robeck and others (1962-b) suggest that effluents from a septic tank can be degraded from ABS levels of 5 or 35 ppm to less than 0.5 ppm if applied properly to certain unsaturated soils; to achieve these results the dosing of soil must be intermittent for proper aeration conditions, necessary to this biodegradation. The results of these authors on unsaturated flow are encouraging but fail to explain the vast amount of water pollution from ABS discharge from septic tanks; it is also dubious if a septic tank could be made to operate along lines parallel to their laboratory studies.

Studies have been made on the adsorption of ABS on quartz grains with and without bacterial slime growth to determine the influence of this growth on ABS adsorption (Ewing and others, 1961). These investigators found that solutions containing 50 ppm of ABS adsorbed 3.3 µg/g and 22.3 µg/g on clean sand surfaces and covered with slime sand, respectively, and concluded that bacterial slime significantly enhances adsorption capacity of sand columns. In another study on the filtration of polluted river water through the Bunter Sandstone soil (Wheatland and Borne, 1961) containing 13,000 to 100,000 total bacteria and 120 to 760 coliform bacteria per ml it was shown that this soil removed from 81 to 96.5 percent of both types of bacteria.

One of the most significant studies on removal of ABS by percolation of sewage-like water through five types of agricultural soils common in California has been recently reported (Klein and others, 1961). These investigators percolated various ions normal to sewage effluents, together with ABS and tracer amounts of ABS^{35} through 25 cm long soil columns and made the following conclusions:

(1) All soils examined displayed an ability to adsorb ABS, the adsorption being greatest in the top zone of the soil column, probably as a result of selective entrapment of the larger ABS molecules. (ABS used in the study contained 12 to 16 carbon atoms in the alkyl chain.)

(2) The most adsorptive soils were those with the most uniform gradation of particle sizes.

(3) In soil columns 25 cm deep and 2.5 cm in diameter, the most adsorptive soils removed 50 percent of the ABS present in the first liter of liquid percolated through it. The range for various soils was from 22 to 66 percent. After 5 liters, only about 5 percent of the influent ABS was removed.

(4) There was virtually no difference between the biologically active and biologically inactive soils in their ability to adsorb ABS under conditions of either saturated or unsaturated flow. This finding is contrary to that of Ewing and others (1961).

(5) Some bio-degradation of ABS occurred during periods of biologically active unsaturated soil, but the rate was too small to be of consequence in preventing complete elimination of ABS; the build up of ABS from adsorption was hundreds of times that amount broken down by biodegradation. Biodegradation was confined largely to the top one inch of the soil column. This observation does not support, entirely the findings of Roebeck and others (1962-b)

(6) In the range of concentrations of ABS used in the experiments (0.001 to 10.0 ppm) adsorption on soils was directly proportional to the ABS concentration in the infiltrating liquid; and observation in accord with the Freundlich adsorption isotherm as found by us in our report.

(7) Eighty percent of the adsorbed ABS was readily leached from the soil by detergent (ABS)-free water. Continual application of leaching water produced a further slow reduction in ABS content of the soil down to some minimum residual value.

(8) The degree of adsorption of ABS on soils is insufficient to prevent ABS from penetrating to ground water in terms of times required for waste water disposal projects.

Much of the data reported by the California investigators is in excellent agreement with data supplied in this report.

In our study the filtration characteristics of a primary sewage effluent (Denver, Colorado, treatment plant) through various packed soil columns were investigated. The test columns consisted of Lucite cylinders approximately 4 feet (column 1), 2 feet (column 2), and 1 foot (columns 3 to 9) long and 3.75 inches inside diameter. The various columns were packed with materials shown in table 21. Column 3 (not listed in table 21) was packed with colliodal alumina ("Baymal") coated 20–30 mesh Ottawa sand. The material in the columns was packed with a mechanical vibrator (Morris and Kulp, 1960). To simulate ground water flow rates, the effluent was maintained at approximately 2 ml per minute by peristaltic pumps giving average flow rates through the columns that ranged from 1.99 to 3.67 feet per day (table 21). The sewage effluent was introduced at the base of the columns and filtered upward to minimize the effects of air entrapment and channeling. The apparatus for column 1 is shown in figure 82. The sewage effluent flowed by gravity to the peristaltic pump and was subsequently forced to flow through the column with the column effluent being discharged at the top into a 2 liter graduated cylinder. Tygon tubing was employed throughout to connect the component parts of the system.

Determination of selected constituents and properties of sewage effluent (before filtration) over a two-year period indicated the following ranges of concentration: total bacteria, 160,000 to 5,000,000 per ml; ABS, 3.3 to 5.5 ppm; dissolved solids, 440 to 1,000 ppm; dissolved oxygen, 0.0 to 5.0 ppm; biochemical oxygen demand, 125 to 225 ppm; pH, 7.4 to 8.1; and surface tension, 50 to 55 dynes per centimeter. ABS was determined by the methylene-blue method, which is subject to a variety of limitations (Wayman, 1962-a). Determinations of coliform and total bacteria were made by the pour-plate technique, using Mac Conkey and Nutrient agars, respectively, at an incubation temperature of 37°C for 48 hours. Other determinations were made by standard laboratory methods.

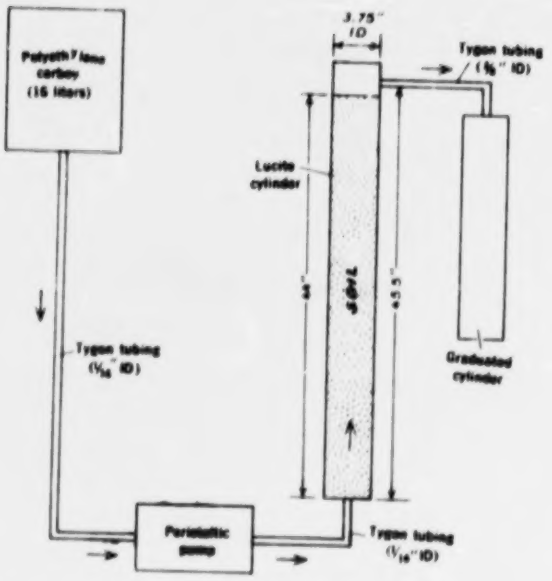


Figure 82.—Sketch showing filtration apparatus for column 1.

The size distribution data of the various soils is presented in figure 83 based on sieve analyses using Tyler standard sieves. Other soil-column characteristics are given in Table 21. Porosity of the packed soils was determined by measuring the volume of fluid required to saturate the measured volume of packed soil. This porosity compared favorably with that calculated from volume and weight of packed soil. The pH of each soil was determined by suspending 1 gram of soil in 5 ml of distilled water (pH 6.4) for 30 minutes before taking the pH reading.

The mineralogical constituents of each of the soils was determined by combined microscopic and x-ray diffraction techniques. Table 22 shows the major mineral constituents identified. The numbers under the various soil columns represent the relative amounts of the various minerals. The number 1 shows the highest concentration of a constituent with decreasing amounts of other constituents as the numbers become larger than 1.

Figure 84 shows the amount of removal of selected constituents of sewage effluent with time for column 1 (Ottawa Sand). This column

Table 21.—*Characteristics of soils used in ABS filtration studies.*

	Column 1 20–30 mesh Ottawa sand (coarse sand)	Column 2 Brighton soil (sandy loam)	Column 4 Muck (silty sand)	Column 5 greensand Marl (fine-med. sand)	Column 6 Hornblende-schist soil (med.-fine sand)	Column 7 Basalt soil (silty sand)	Column 8 Loess (sandy silt)	Column 9 Adobe (medium-fine sand)
Soil volume (cc)	7,750	3,400	1,600	1,600	1,600	1,600	1,600	1,600
Total time of operation (days)	71	72	37	26	22	22	21	21
Total fluid volume (liters)	205	168	88	58	65	60	62	58
Average flow rate (ml/min.)	2.0	1.63	1.64	1.56	2.06	1.88	2.18	2.00
Average flow rate (ft/day)	3.67	2.16	1.99	2.32	2.80	2.79	3.35	2.79
Median grain diameter (microns)	760	50	280	380	320	150	50	290
Corfficient of sorting (So)[1]	1.02 (very well sorted)	2.96 (very poorly sorted)	2.83 (very poorly sorted)	1.43 (moderate sorting)	2.24 (very poorly sorted)	3.16 (very poorly sorted)	1.61 (poorly sorted)	2.02 (poorly sorted)
Surface area (cm^2/g)[2]	100	10,500	3,650	600	1,950	6,100	11,500	1,200
Porosity, packed (percent)	39	53	58	47	52	47	46	50
Total soluble salts (ppm)	N.D.[3]	1,400	N.D.	N.D.	N.D.	N. D.	N.D.	N.D.
Organic matter (ppm)	0	27,400	572,000	6,400	4,900	22,700	1,400	1,460
$CaCO_3$	N.D.	2,000	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P_2O_5 (ppm)	N.D.	280	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
N as NO_3 (ppm)	N.D.	12	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Available K (ppm)	N.D.	130	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
pH	6.7	7.3	7.1	3.4	5.7	6.2	8.4	8.7

[1] Trask, P.D., 1930, Mechanical analysis of sediments by centrifuge: Econ. Geology, v. 25, p. 581–599.
[2] Calculated from sieve analysis.
[3] Not determined.

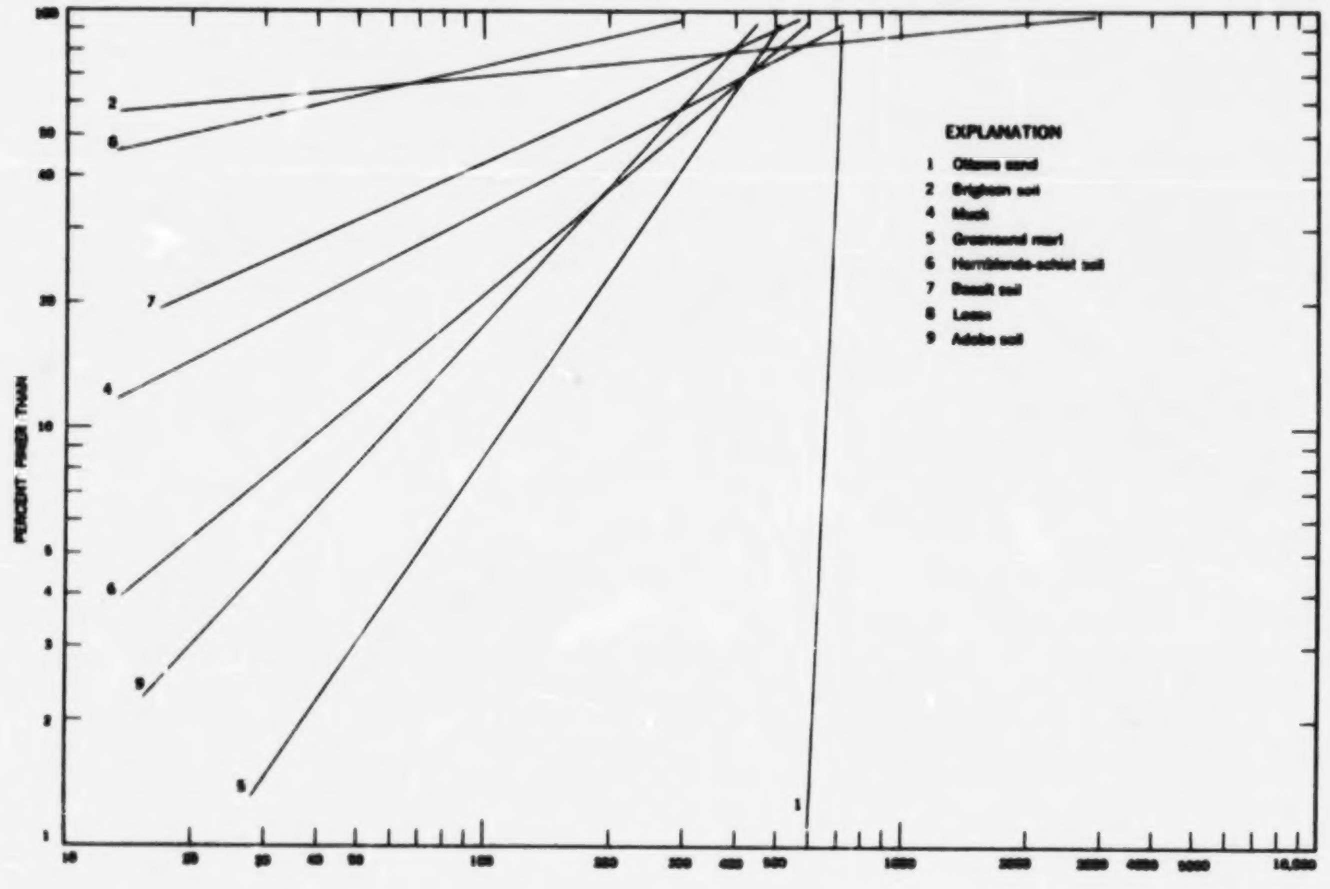


Figure 83. —Size distribution data on various soils used in filtration studies.

Table 22.—*Mineral constituents of various soils.*

Mineral	Column							
	1	2	4	5	6	7	8	9
Quartz	1	1	1	2	1	1	2	2
Illite	---	4	---	1	4	---	---	5
Clay	---	2	3	3	6	---	---	4
Feldspar	---	3	2	---	---	2	3	3
Dolomite	---	---	5	---	---	---	1	---
Calcite	---	---	4	---	---	---	---	1
Chlorite	---	---	---	---	3	3	4	---
Hornblende	---	---	---	---	2	---	---	---
Fluorite	---	---	---	---	5	---	---	---

Column

1-Ottawa Sand
2-Brighton Soil
4-Muck
5-Greensand Marl
6-Hornblende-Schist

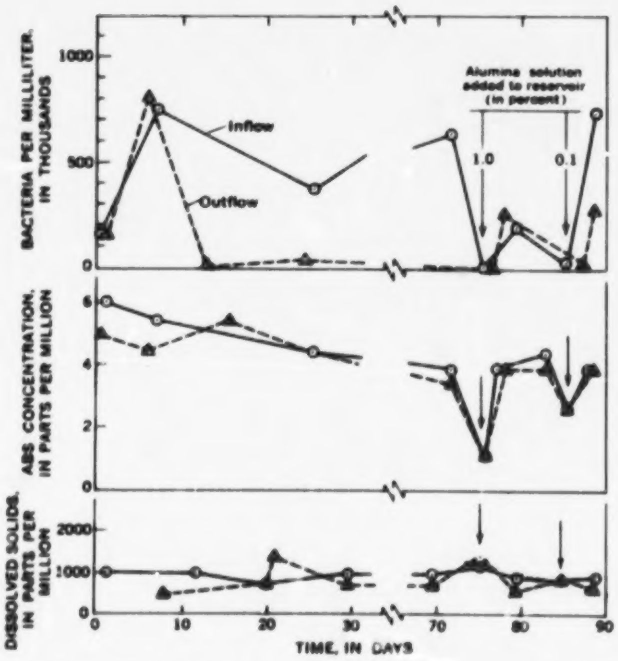


Figure 84. —Typical effects of soil filtering of sewage effluent with time.

was operated continuously for 71 days. During the first 10 days of operation, bacteria traveled through the column virtually unaffected. During the next 61 days, the removal of bacteria by filtration ranged from 50 to 99.8 percent and averaged about 88 percent. Filtration, however, had little influence on the ABS and dissolved-solids contents (figure 84). After 71 days of operation, a 1 percent solution of a positively charged colloidal alumina ("Baymal") was added to the sewage reservoir. The colloidal alumina immediately caused flocculation of about 70 percent of the negatively charged ABS and reduced the bacterial count in the reservoir to zero. No additional ABS was removed by percolating this alumina-containing solution through the soil column. Addition of a 0.1 percent alumina solution removed most of the bacteria but was only about half as effective as the 1 percent solution in removing ABS (figure 84). Although effective, use of an alumina solution to treat sewage effluent on a large scale would be economically prohibitive at the present cost of 16 cents per gallon of treated water. Figure 85 shows the effects of figure 84 on the basis of amount of sewage effluent filtered per cubic foot of sand. Negative values of percent removal indicate that the constituent increased above that in the inflow solution. It is significant to indicate the amount of removal of dissolved solids and ABS which was previously adsorbed on the sand. This removal may have resulted from the release of dead bacterial cells from the sand grains to which dissolved solids and ABS were adsorbed. Thus, contaminants may eventually get into ground water after being removed by sand through release of dead bacterial cells to which these substances were previously adsorbed.

Figure 86 shows the filtering effects by the sandy loam (Brighton Soil, Column 2). Column 2 was operated for 72 days. Chemical analyses of effluent (column outflow) sampled during initial operation of the column indicated that the dissolved solids content of the sewage had increased markedly in passing through the column. This increase presumably resulted from flushing (leaching) of a portion of the high content of organic matter in the soil (table 21). The amount of dissolved-solids increase was so severe that ABS analyses were impossible for about the first 20 gallons of sewage effluent pumped through the column (figure 86). After the first day of operation, the amount of bacteria removed ranged from about 60 to 96 percent and average 93 percent. The amount of ABS and dissolved solids removed even after 72 days of column operation was insignificant.

Column 3 consisted of 20–30 mesh Ottawa sand coated with colloidal alumina and had a porosity of 34 percent. The column was operated for only 3 days. Initial operation removed 99 percent of the ABS. However, after 1½ days of operation, the capacity of the column to remove bacteria and ABS decreased markedly and the test was terminated.

Figure 87 shows the filtering effects of the sewage effluent by muck. This column was operated for 37 days for studies on ABS removal and 22 days for removal studies on the other constituents. This soil had the most significant effect on the removal of ABS. The amount removed average about 90 percent for the first 500 gallons per cubic foot of flow; at this point the percent removal continuously decreased with volumetric throughput down to about 30 percent. The data on adsorption studies of ABS and column studies do not give a very satisfactory agreement with respect to the expected percent removal. Other factors in such organically rich soils must also influence this removal but could not be evaluated in the study. The removal of coliform bacteria by the muck was quite erratic probably as a result of the high original bacterial content of muck as indicated by increased amounts of bacteria flushed out (figure 87). The amount of dissolved solids removed increased with the amount of sewage placed through the column but the absolute amount removed up to 220 gallons/ft^3 was insignificant; up to 100 gallons/ft^3 continuous leaching of dissolved solids from the muck was observed. No significant change in pH with amount of volume throughput was observed. Thus, high organic soils seem to be desirable for removal of ABS from waste solutions but possess deleterious effects with respect to removal of bacteria and dissolved solids.

Figure 88 shows the filtering effects of sewage effluent by greensand marl. This soil had a significant influence on removal of ABS; for the first 100 gallon per cubic foot of flow about 70 percent of ABS was removed which decreased to 30 percent with subsequent volume throughput. The high capacity of this soil for ABS removal can be attributed to its acidic nature, the pH of this soil suspension being 3.4. Thus, a certain amount of

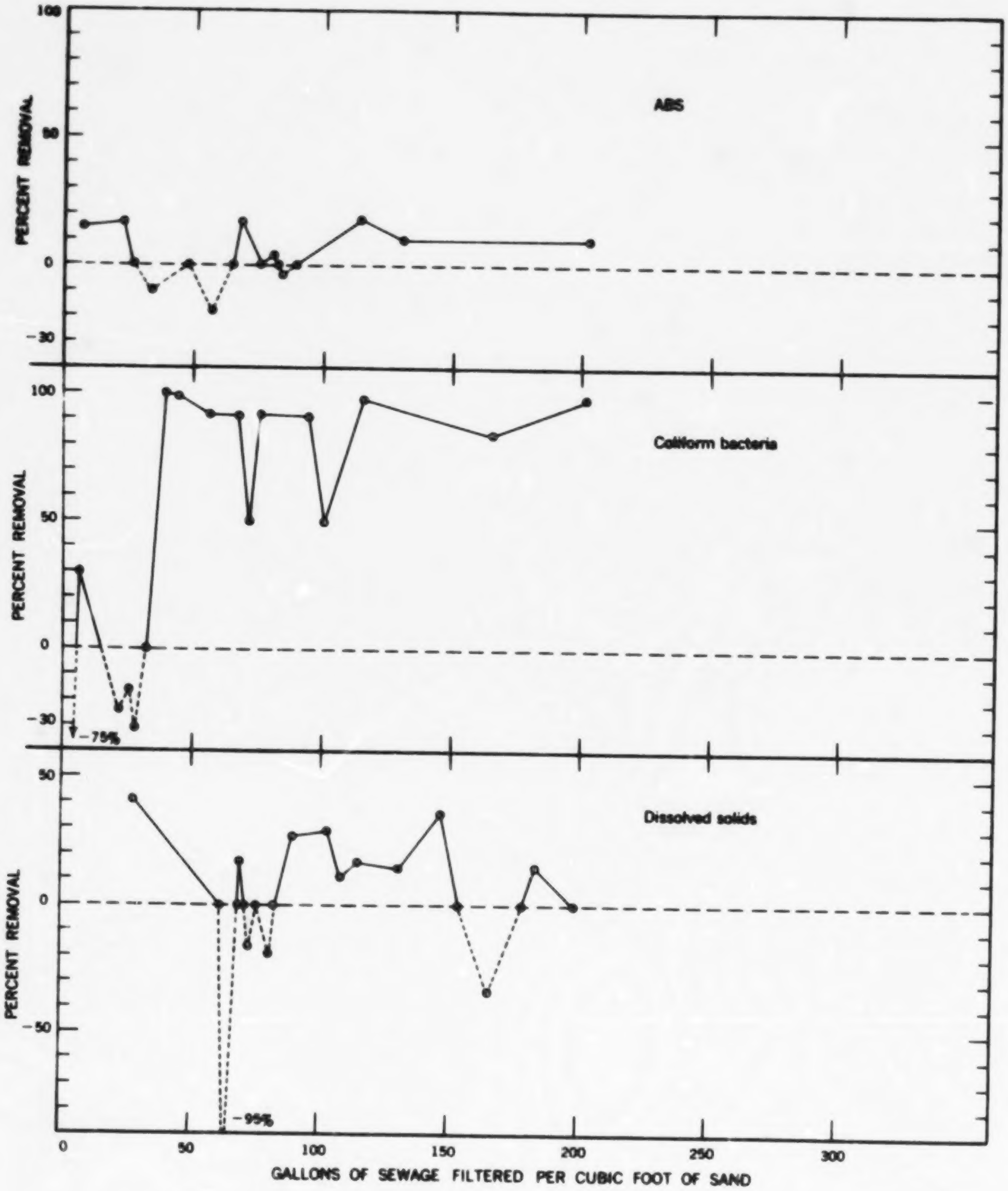


Figure 85.—Percent removal of ABS, coliform bacteria, and dissolved solids in sewage plant effluent with respect to gallons filtered per cubic foot of Ottawa Sand.

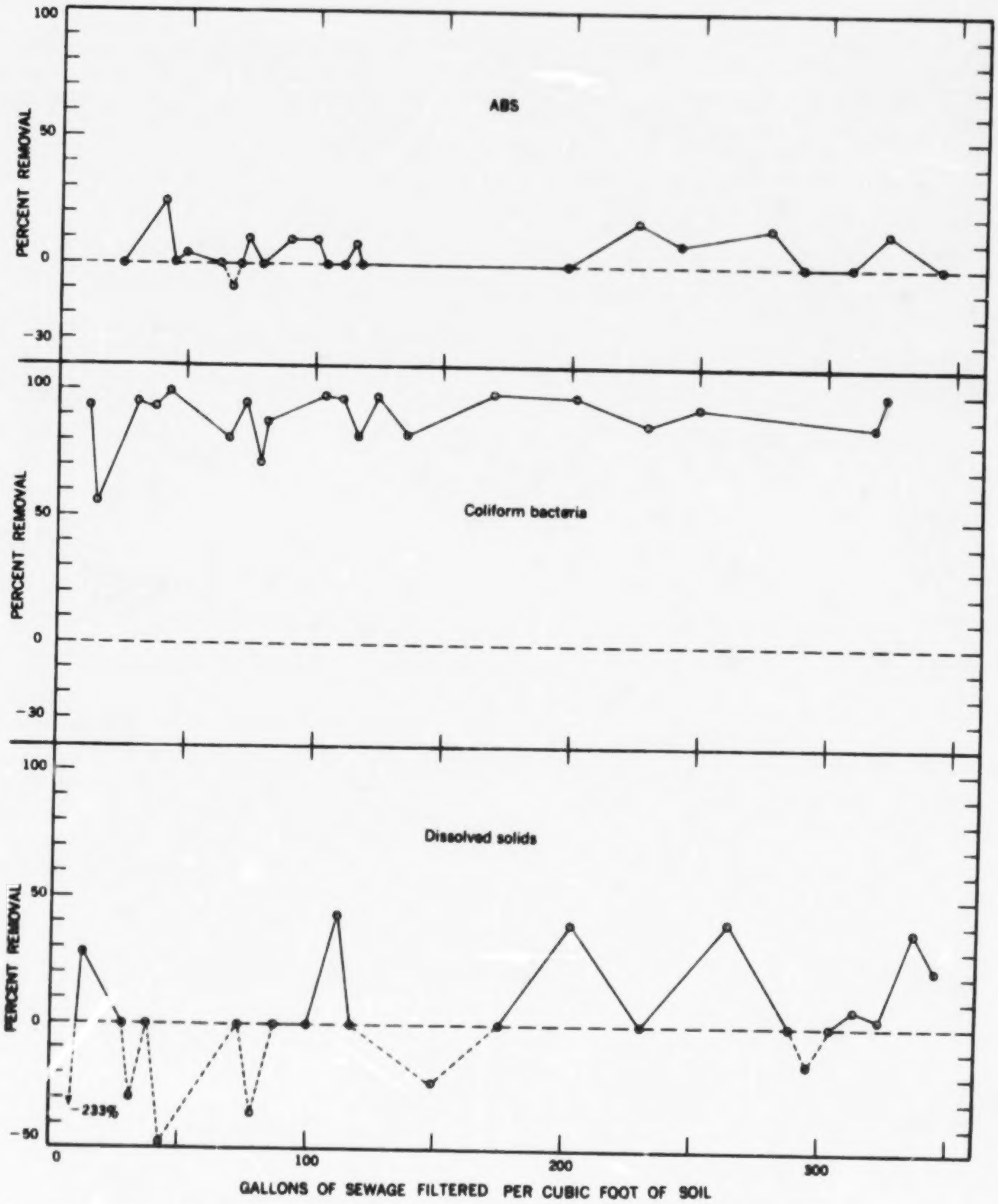


Figure 86. —Filtering effects of ABS, coliform bacteria, and dissolved solids in sewage plant effluent by sandy-loam, Brighton Soil.

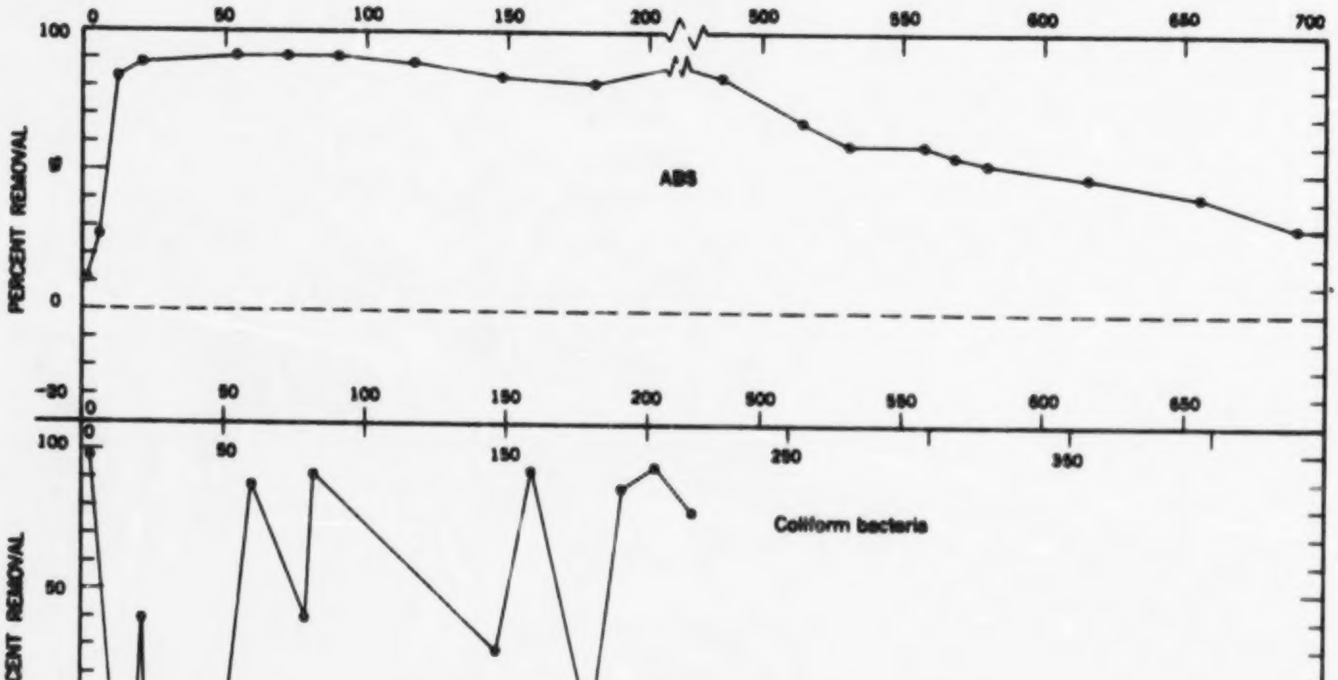


Figure 87. —Filtering effects of ABS, coliform bacteria, and dissolved solids in sewage plant effluent by muck.

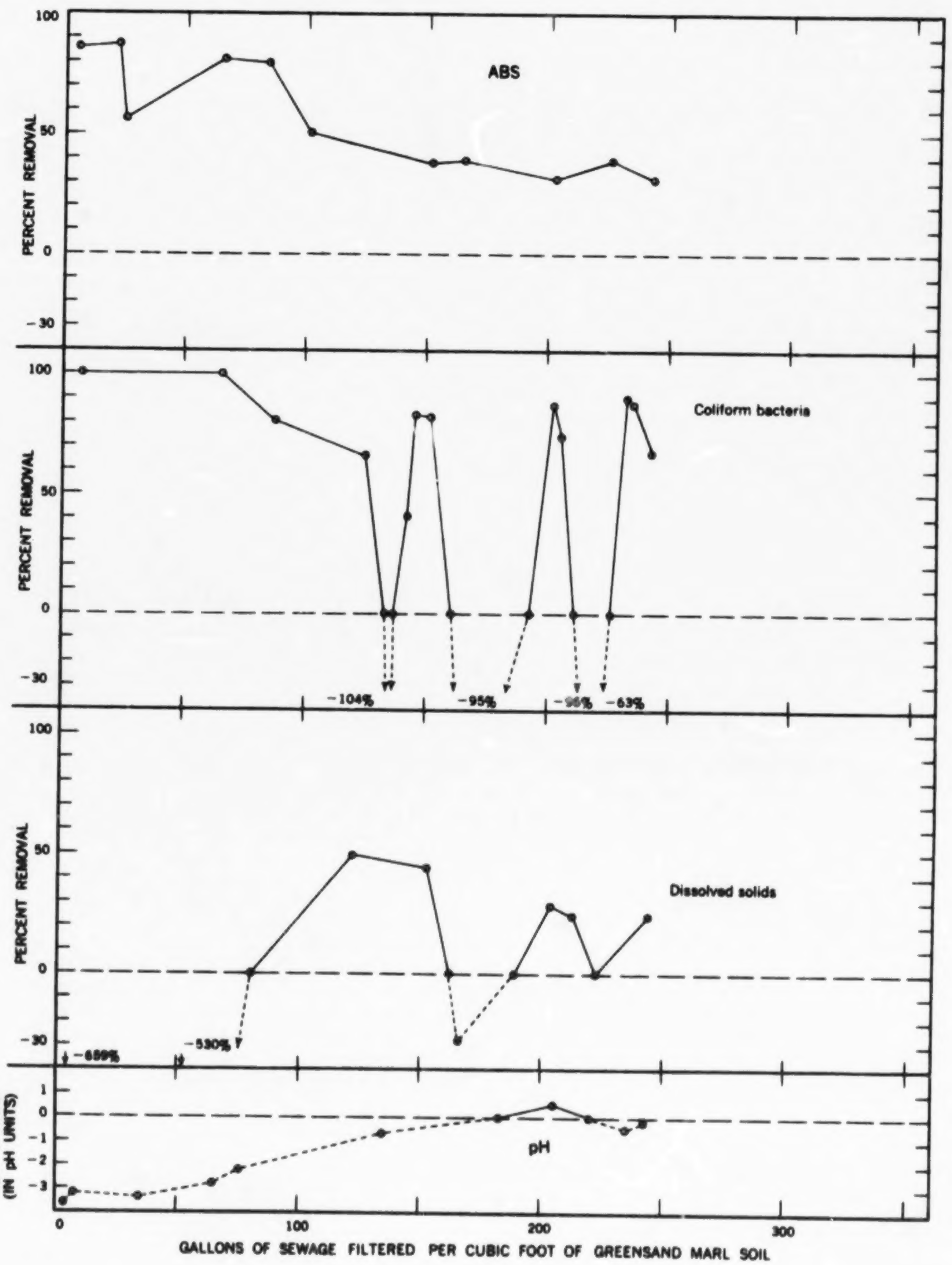


Figure 88. —Filtering effects of ABS, coliform bacteria, and dissolved solids in sewage effluent by greensand-marl.

acidic constituents are readily leacheable from such soils which enhance ABS removal. The tendency to remove total dissolved solids and coliform bacteria is quite erratic with increased amounts of sewage effluent throughput.

Figure 89 shows the filtering effects of constituents in sewage effluent by basalt soil. The affinity of this soil for ABS and dissolved solids is similar to the greensand marl with high initial adsorption which decreases with the amount of effluent throughput. Significant amounts of coliform bacteria can also be removed which can be subsequently desorbed as shown by the break in this curve (figure 89).

Figures 90 to 92 show the filtering effects of constituents in sewage effluent by hornblende-schist, loess, and adobe soils. These soils show similar tendencies to remove ABS with amount removed decreasing rapidly with amount of volume throughput. The removal of bacteria of all three soils is quite erratic with amount of infiltrating liquid. Hornblende-schist soil shows the best tendency to remove dissolved solids (figure 90), whereas, significant amounts of dissolved solids are leached from the loess and adobe soils (figures 91, 92).

Bacterial-slime growth, which resulted in pore clogging, was indicated in all columns by darkening of the filter media, presumably largely by iron sulfide (FeS) (Winneberger and others, 1960). In fine-grained soil, pore clogging apparently develops in an erratic pattern along the more permeable channels (figure 93). After terminating the tests on fine-grained soils, the columns were split open and visual examination indicated erratic penetration and development of bacterial growth throughout the column. Much of the growth was confined to the extermal portion of the packed soil, which revealed significant amounts of algal colonies. Appreciable amounts of gases were also generated in the columns under these anaerobic conditions, presumably mainly as methane (CH_4) and dihydrogen sulfide (H_2S); the effects of these residual gases on column appearance is shown for a portion of the Brighton soil (figure 94) with the gaseous inclusions within the soil. Pore clogging became so severe in some of the fine-grained columns that portions of the column became severed from others; the generation of anaerobic gases also probably aided in these separations. In fine-grained soils these column separations occurred between 15 to 68 days. Pore clogging and discoloration of sand-grains (Ottawa Sand) is shown after 71 days of operation along with the color of the original sand (figure 95). In this coarse sand, pore clogging as shown by discoloration seemed to occur in a uniform manner in the direction of sewage effluent flow. After 71 days of operation, pore clogging was minor in this sand in comparison to the finer-grained soils. The observations mentioned above allude to the possible problems of surface penetration from waste solutions in fine-grained soils as a result of bacterial clogging of pores.

Because waste-solutions contain surfactants like ABS and others, it is significant to pose the question: DO SURFACTANTS INCREASE THE INFILTRATION RATES OF WATER IN POROUS MEDIA? In a previous study, surfactants in solution flowing between coarse sands increased infiltration, but in fine-grained, clayey sands surfactants decreased flow of water probably as a result of adsorption effects in pore clogging with reduced capillarity (Plegat, 1961). In another study (Wilkinson and Klute, 1962), it was concluded that the principle force acting on water in the 104 to 149 μ (micron) sand is that resulting from pressure gradients associated with surface-radius of curvature effects; in the 53 to 74 μ sand and the 13.0 to 18.5μ silt, forces other than those attributed to surface tension must be involved. It is well known that soils are difficult to wet in an air-dry state but can become water wet if surface tension of water is lowered. Particle coatings on soils from hydrophobic substances such as olive oil, palmitic acid, and oleic acid are also believed to cause water to be repelled from soils (van't Woudt, 1959); this in effect would increase infiltration rates through soil. An equation relating the rate of liquid infiltration into a soil to the physical properties of the liquid, effective pore radius, and solid-liquid contact angle assuming Poiseuille's approximation for cylindrical tubes has been derived as (Letey and others, 1962):

$$Q = \frac{Cr^2 \rho g h}{8L\eta} + \frac{2Cr\gamma \cos\theta}{8L\eta} \qquad (85)$$

η = liquid viscosity

where

Q = quantity of liquid entering the soil per unit surface area per unit time

C = volume fraction of the soil which is (wet) porosity

r = effective pore radius

ρ = liquid density

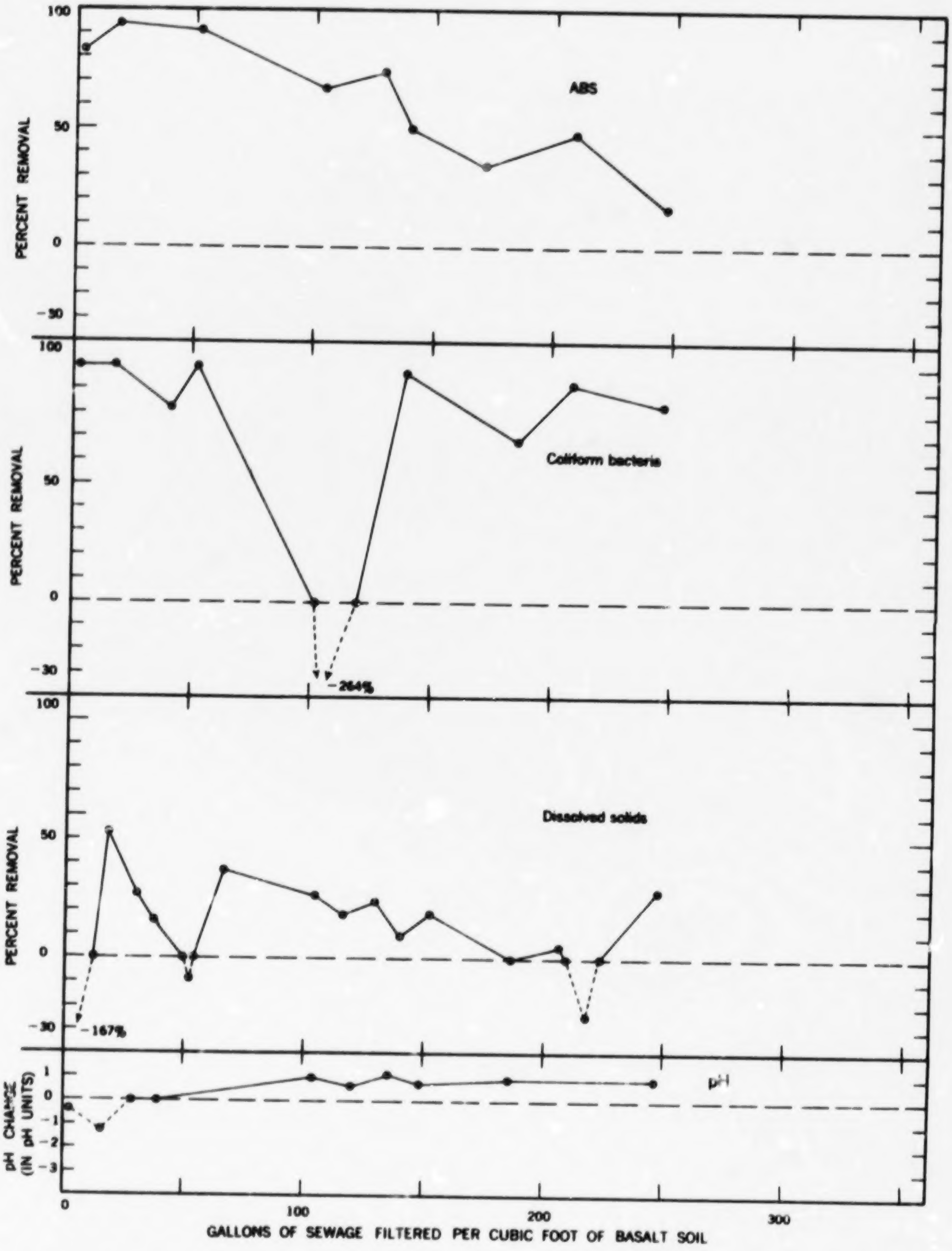


Figure 89.—Filtering effects of ABS, coliform bacteria, and dissolved solids in sewage effluent by basalt soil.

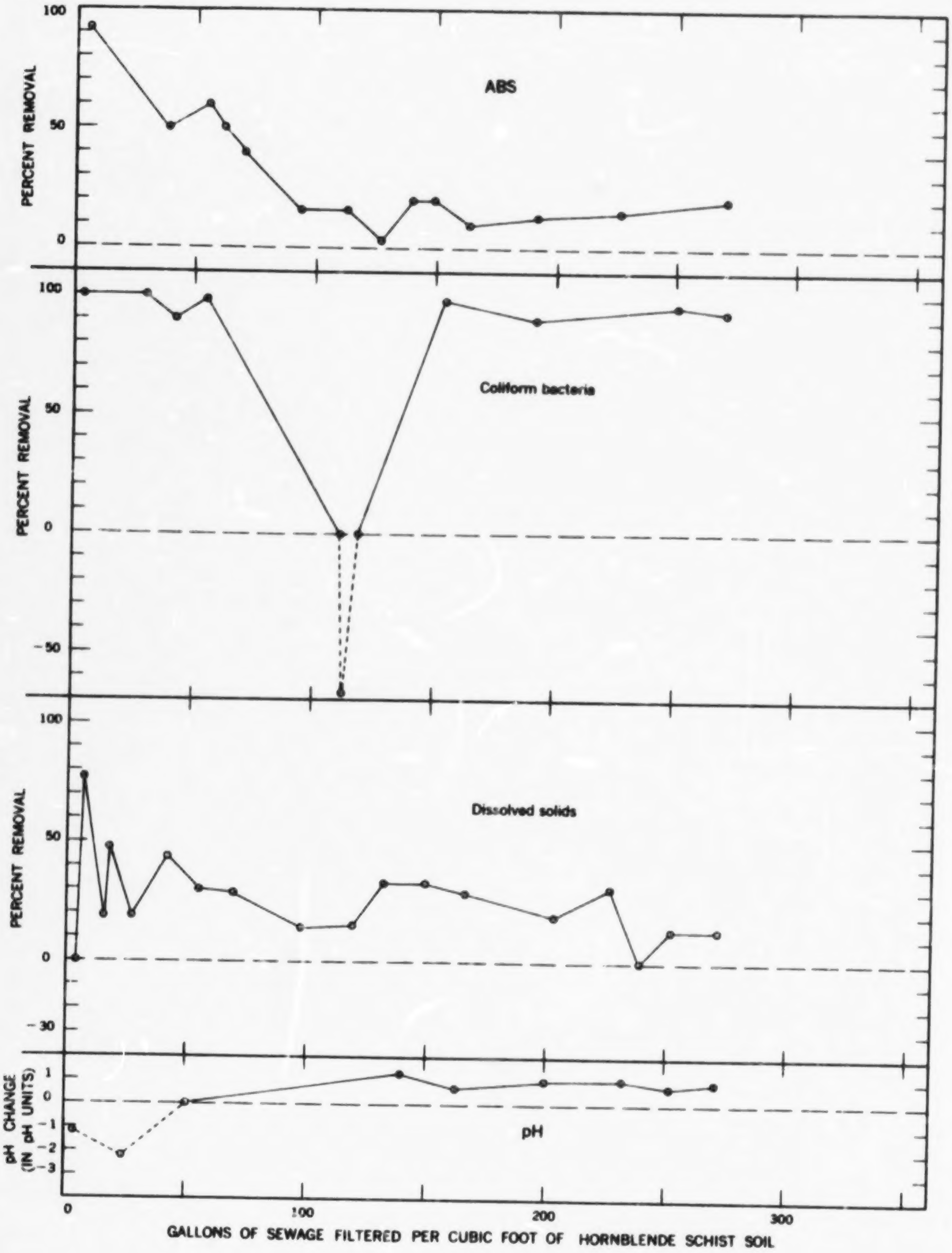


Figure 90.—Filtering effects of constituents in sewage effluent by hornblende-schist soil.

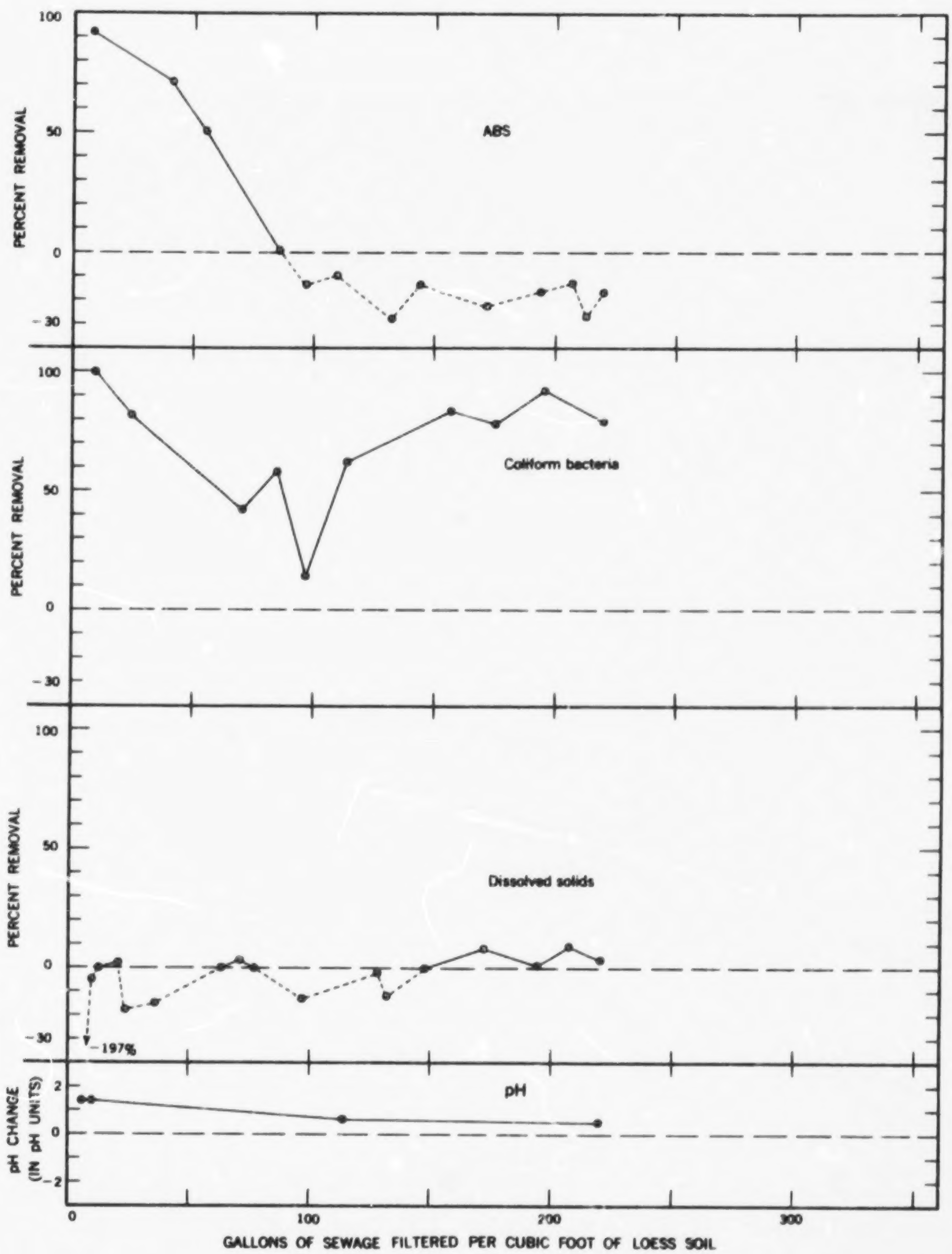


Figure 91.—Filtering effects of constituents in sewage effluent by loess soil.

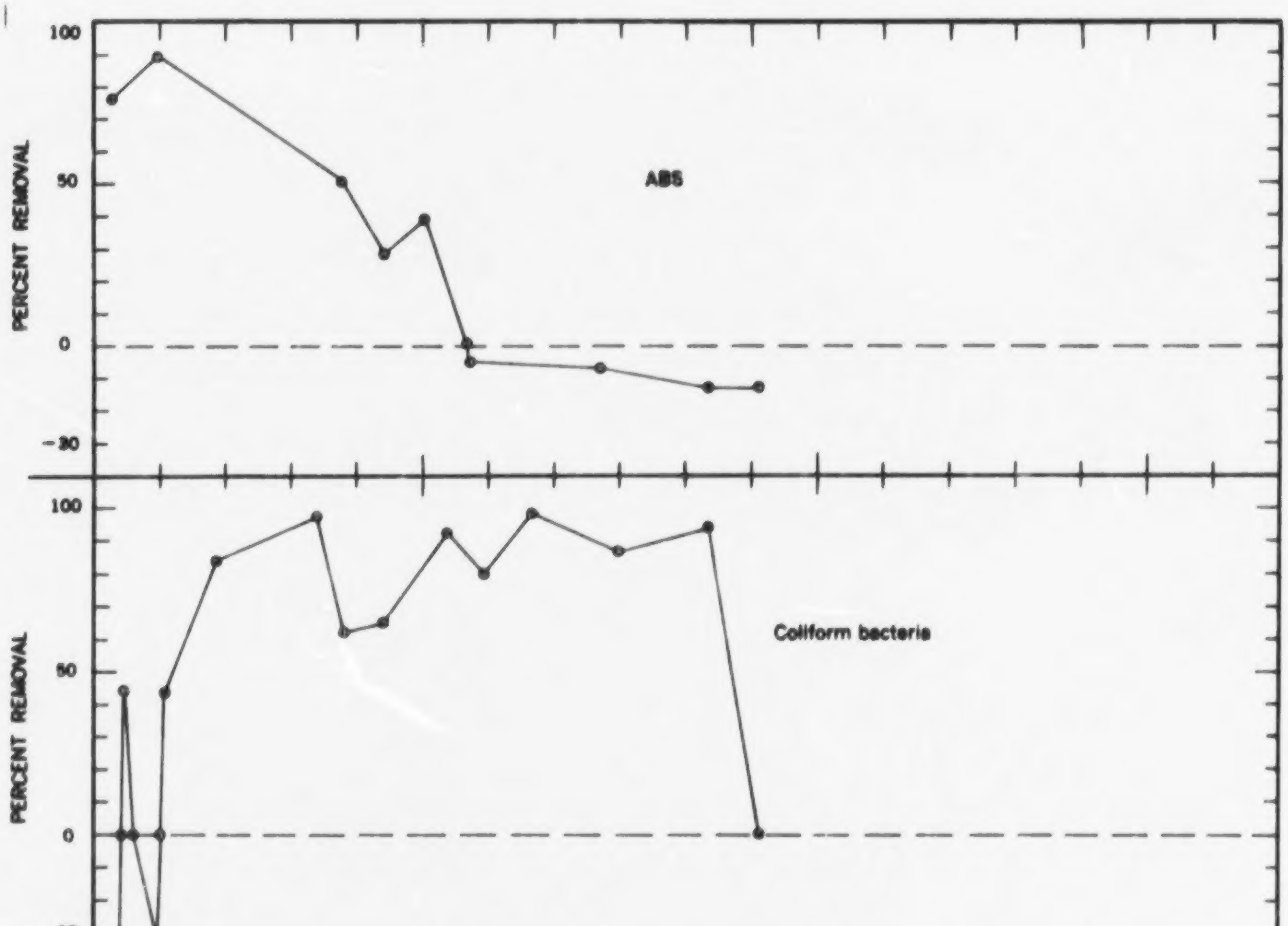


Figure 92. —Filtering effects of constituents in sewage effluent by adobe soil.

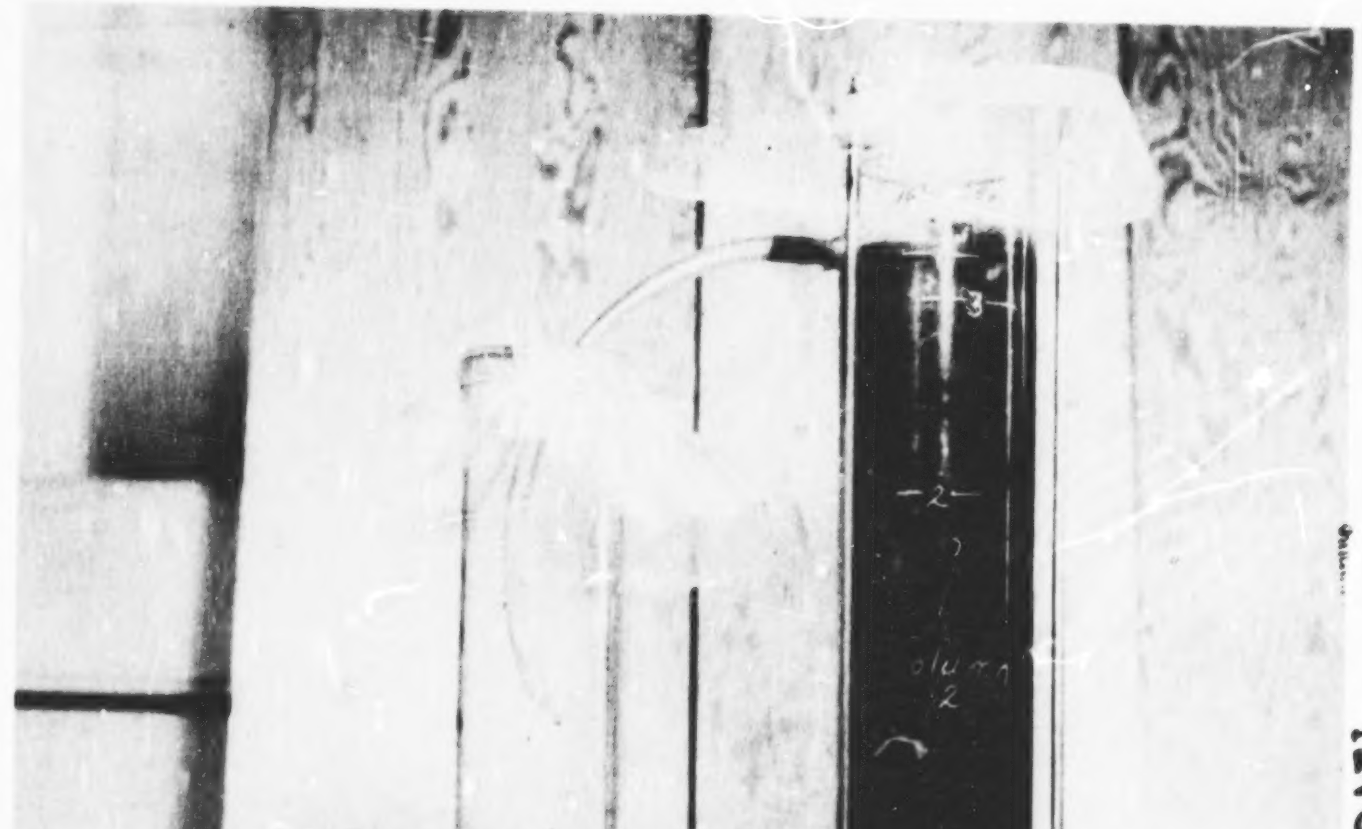


Figure 93. —Photograph illustrating pore clogging (bacterial growth) along permeable channels of sandy-loam (Brighton Soil).

NOT REPRODUCIBLE

NOT REPRODUCIBLE

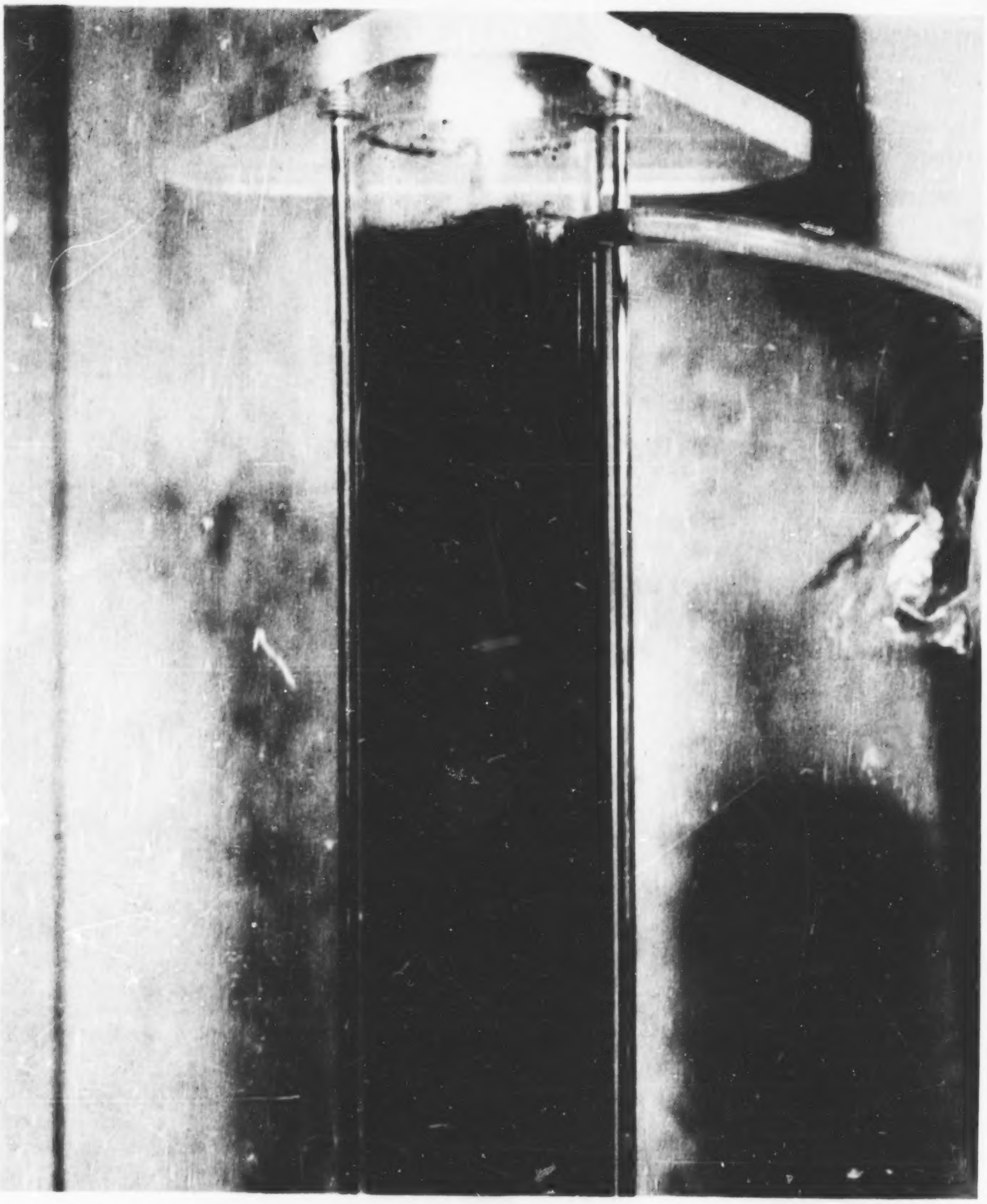


Figure 94.—Photograph illustrating the formation of gases in Brighton soil column under anaerobic conditions.

NOT REPRODUCIBLE

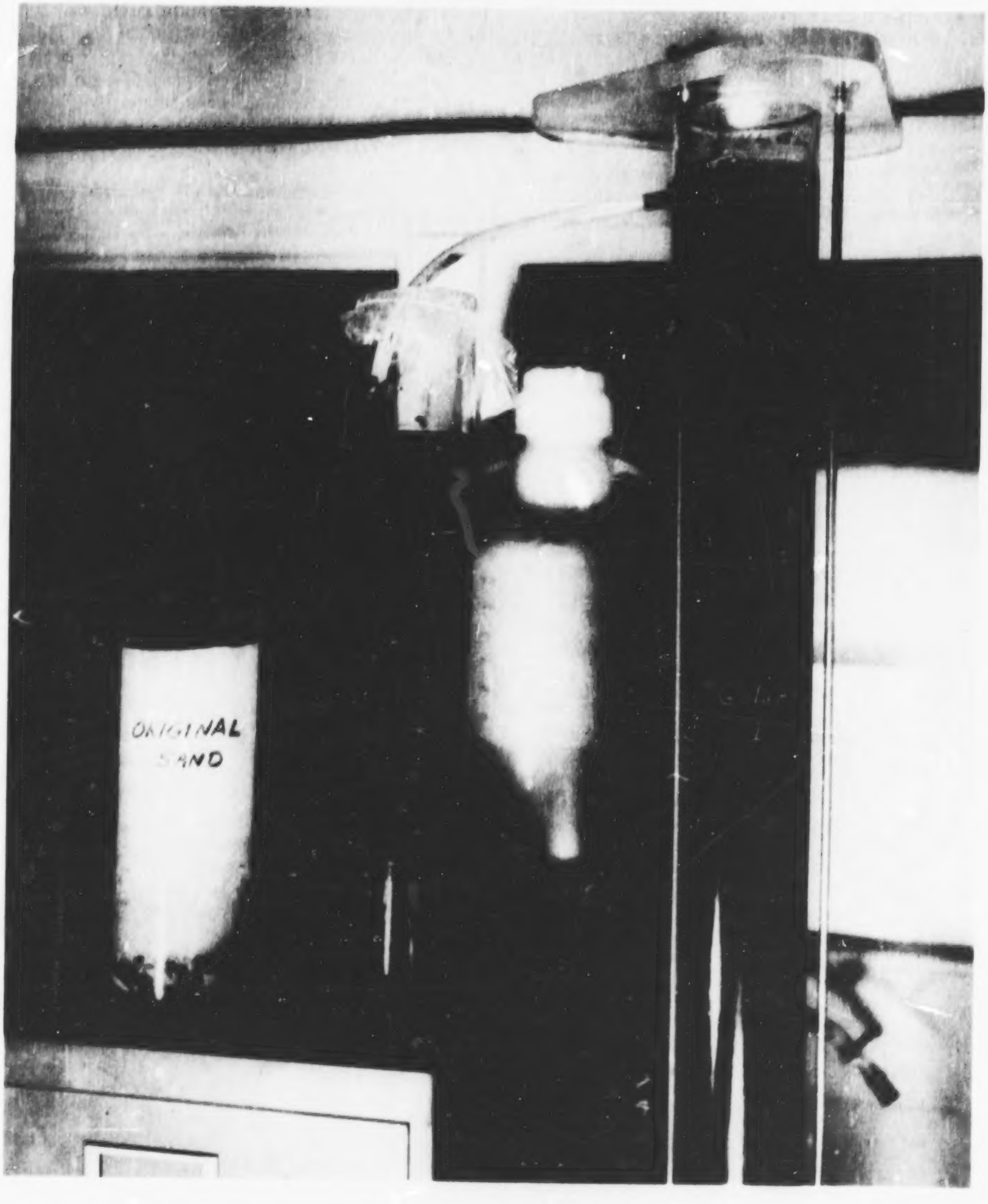


Figure 95. —Photograph illustrating the discoloration of Ottawa Sand by bacterial growth after 71 days of operation.

g = gravitational constant
h = length of liquid column (distance from water surface to wetting front)
L = length of wet column (distance from the soil surface to wetting front)
n = liquid viscosity
γ = liquid surface tension
θ = liquid-solid contact angle

There are a number of interesting but yet speculative points that may be deduced from (85). If the size of soil particles becomes smaller, r^2 becomes smaller and C would most likely be reduced because of poor wetting (liquid penetration) and Q would decrease (decrease in infiltration rate) because of the first term of the equation. The second term in (85) could be used to predict that a decrease in surface tension decreases infiltration rate whereas, a decrease in the solid-liquid contact angle would increase the infiltration rate; however, when surfactants are in solution and in contact with solids, both parameters are decreased. Thus, the parameter which is most influencial would seem to control the infiltration rate. In actual practice the nature of surfactant adsorption (retention) by the soil particle must be considered. When surfactants are sorbed by soils, soils become more hydrophobic (water-repellent) from these surface films; under these conditions infiltration rates should increase. If subsequent infiltration can remove the hydrophobic films by mechanical desorption, then the soil surface becomes more hydrophilic (water-affinity) and infiltration rates should decrease. Thus, in nature both hydrophobic and hydrophilic films are probably present on soils. Certain studies on infiltration of ABS into California soils (Klein and others, 1961) indicated that ABS is adsorbed and later desorbed by subsequent water infiltration; it can be inferred from this work that both types of surfaces occur on soils as a result of ABS. In another recent study (Pelishek and others, 1962) it was shown that wetting agents (surfactants) can increase infiltration rates into hydrophobic soils but have either no effect or adverse effects on soils which are not particularly hydrophobic. This aspect of water pollution offers challenging research efforts and is essentially uninvestigated.

From the studies on filtration of a primary sewage effluent by various soils, the following conclusions can be made:

(1) Most soils removed over 90 percent of bacteria from sewage within a few feet of travel, which contributed to severe clogging in the finer-grained soils. With some soils, bacteria seem to be desorbed with amount of volume throughput; ABS and other constituents attached to such slimes would also be desorbed.

(2) ABS can be removed significantly with initial infiltrating effluent but additional effluent throughput has insignificant amounts of ABS removed. Ottawa Sand and sandy loam had little tendency to remove ABS but some of the less common soils are effective ABS filters such as muck, basalt, and greensand-marl.

(3) Dissolved solids moved through the columns virtually unaffected with respect to removal.

(4) In general, the criteria used to account for adsorption of ABS on minerals can be applied also to soils but additional hydraulic and bacteriological factors also influence ABS removal for saturated flow.

GROUND INFILTRATION OF ABS, DISSOLVED SOLIDS, AND COLIFORM BACTERIA FROM RIVER WATER (SOUTH PLATTE RIVER, VICINITY OF DENVER, COLORADO)

In the previous sections of the report, results of both laboratory and pilot studies (soil columns) on behavior of waste solutions or detergents in soil-water environments were given. The present section provides data regarding two important aspects of water pollution in terms of a field study. The specific study involved changes in selected constituents from a discharged sewage effluent in the South Platte River at Denver, Colorado, before and after the discharge point; in addition, pollution of ground water by infiltration from irrigation ditches tributary to the river by ABS, dissolved solids, and coliform bacteria was studied.

The selection of the area for this study was essentially an ideal one. The Denver treatment plant produces a primary sewage effluent, which discharges into the South Platte River a volume of 80 to 100 million gallons per day. Thus, significant amounts of river pollution from constituents in the effluent is to be expected. About one-fourth mile downstream from the discharge point, the river is diverted for the purpose of irrigation water (in ditches) to a large Lake (Barr) and points north of Denver. These irrigation ditches are significant because of their flow over the Brighton sandy loam below which are located various irrigation, domestic, and stock wells supplied from a shallow alluvial aquifer. Thus, both surface water and ground water aspects of pollution can be studied from a major source of pollution (Denver treatment plant).

Surface Water Study

The area was investigated from the period July, 1961, to February, 1963. The location of the area and various sampling points is shown on figure 96 (in pocket). Thirteen surface water samples were taken on a weekly basis over the period indicated above and analyzed for dissolved oxygen (DO), biological oxygen demand (BOD), dissolved solids, total and coliform bacteria, and ABS; average stream flow data were also taken over this period of time. Location of the sampling points consisted of various areas along the South Platte River and the irrigation ditches (O'Brian, Burlington, Fulton, and Beebe) tributary to the river. The most distant point sampled was about 25 miles north of Denver (Fort Lupton) and the area consisted of approximately 60 square miles. In addition to pollution from the Denver treatment plant, five smaller treatment plants (North Washington, Clear Creek, North West Utilities, Adams City, and Brighton) contributed additional but insignificant amounts of pollution to the South Platte River, originating about three miles below the Denver treatment plant.

To assess the effects of pollution of river water from large sewage treatment plants, changes in concentration of selected constituents were compared to concentrations of these constituents prior to the discharge point of the plant along with stream flow data. Figure 97 (in pocket) shows the average change for the year 1962 of various constituents with respect to distance from the point of discharge. Most of the concentrations of constituents measured in the river seemed to be influenced significantly by the discharged sewage effluent. Most of the effects reached equilibrium concentrations in the river within about one mile below the point of discharge except bacteria and streamflow, both of which were probably influenced somewhat by entrance of other streams or sewage effluents into the river below that of the Denver plant. Within about one mile of the discharge point, the following change in measured constituents or parameters was:

+ Streamflow, 310 to 360 cfs
+ ABS, 0.7 to 1.8 ppm
+ Total bacteria, 120,000 to 375,000 per ml
+ Coliform bacteria, 1,000 to 25,000 per ml
+ Biological oxygen demand, 6 to 90 ppm
- Dissolved oxygen, 7 to 3.5 ppm
+ Dissolved solids, 430 to 550 ppm
+ is increase in concentration
- is decrease in concentration

The decrease in D. O. from 7 to 3.5 ppm in the river probably results from the combined effects of (1) increased load of oxidizable organics and (2) lowering of the diffusion rate of oxygen between air and water from increase in concentration of ABS at the air-water interface.

Figures 98 to 100 show variations in certain constituents or streamflow with respect to various times of measurement at selected points on the South Platte River. These data and identical plots at other points were used to construct figure 97. The data for variation

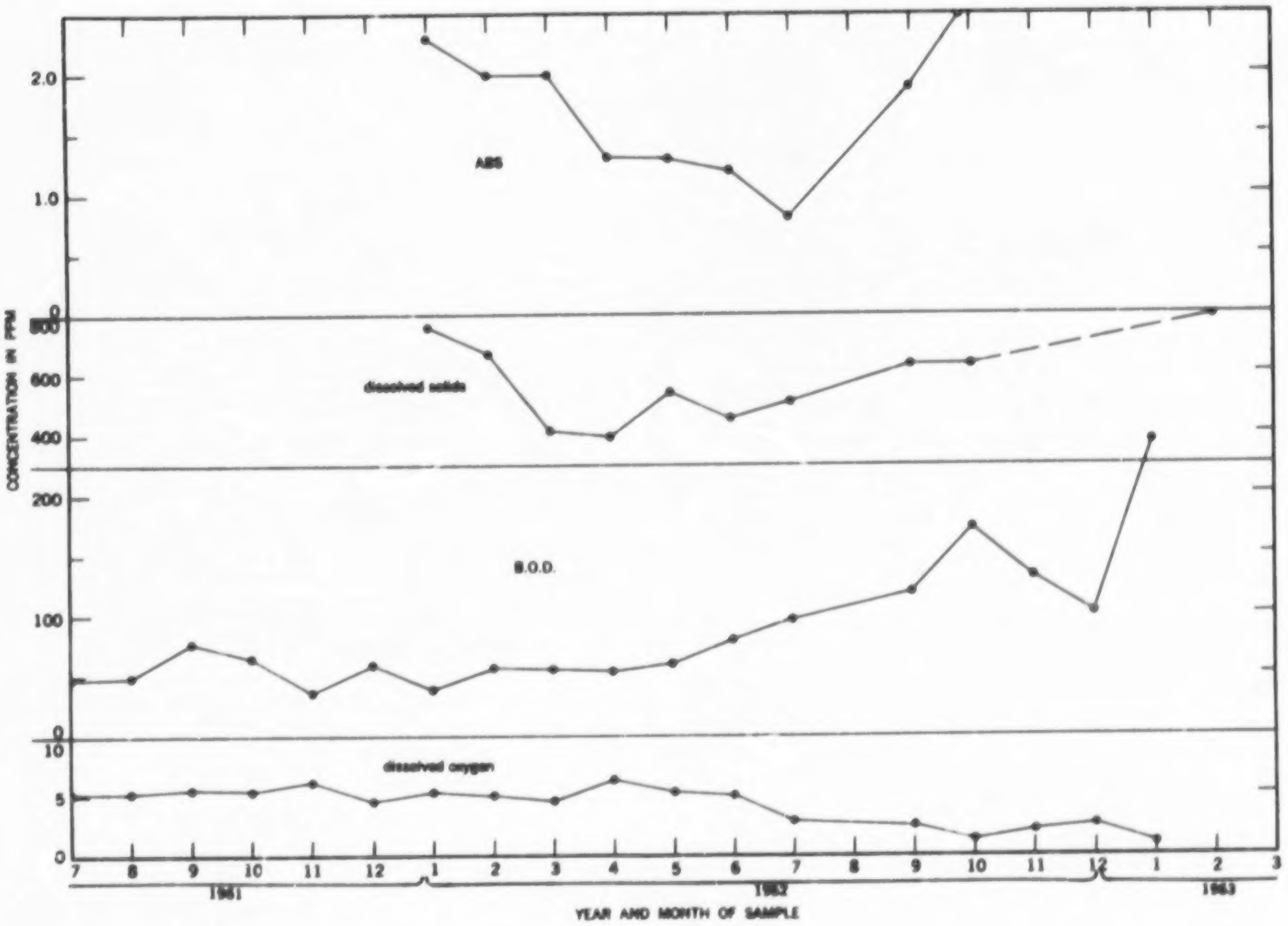


Figure 99.—Variation of ABS, D.O., B.O.D., and dissolved solids 1.1 miles below discharge point of Denver sewage effluent from July, 1961, to February, 1963.

of total and coliform bacteria are shown on figure 101 (in pocket) for the points 0.2 miles above, 1.1 miles below, and 12.75 miles below the point of Denver sewage effluent discharge.

A study of change in concentration of certain constituents in South Platte River has indicated that large sewage treatment plants contribute significantly to the deterioration of water quality of large water bodies. Such constituents are important to a water quality network study and should be monitored along with other chemical or biological species. The evaluation of such parameters are a necessity in determining the feasibility of using such water as a municipal supply or for studies regarding the infiltration of river water into ground water through soils.

Ground Water Studies

Because natural water (polluted) and waste water contain both ABS and bacteria, a portion of the field problem was devoted to determine whether ABS and bacteria migrated from polluted ditch water through soil into ground water without significant removal; it was also of interest to determine whether any relation between ABS and bacterial concentration might exist.

Previous work on the migration of bacteria from waste water through soil has indicated that bacteria may travel significant distances under certain circumstances. In field studies involving pit privies or tile fields from septic tanks, bacteria were observed to penetrate vertically downward to a depth of 5 feet and in some instances to as much as 10 feet (Kliger, 1921). In another field study on latrine trenches, Bacilus coli was found to have penetrated a permeable sand to a depth of 232 feet (Stiles and others, 1927).

In a study of infiltration of human wastes through sandy soil, bacteria traveled easily through the first 5 feet, a few to 15 feet, and occasionally an organism was found to a depth of 35 feet (Caldwell and Parr, 1937). In subsequent studies on this sand coliform bacteria were determined to a depth of 40 feet with a maximum of 80 feet in the wet season (Caldwell, 1937); in more uniform sand, colifrom organisms did not travel beyond 10 feet, while chemical contaminants reached as far as 310 feet (Caldwell, 1938). In a study on sewage spreading through four feet of Hanford sandy loam, coliform bacteria were removed sufficiently to a level acceptable for drinking water standards (Greenberg, 1953). Studies on the injection of sewage into an aquifer (average 4.4 feet in thickness consisting of sand and fine gravel 90 feet below ground surface showed that coliform bacteria moved to as much as 100 feet from the injection well in direction of ground water movement at maximum coliform concentrations of 23 per 100 ml; bacterial penetration decreased with beginning of pore clogging and for a 20 percent sewage water, organisms were reduced at about 19 percent per foot of travel (McGauhey and Krone, 1954). In a rather detailed study on bacterial filtering by soils, the nature of bacterial movement and clogging was found to depend on grain size, temperature, time, and head differential; studies on a laboratory scale and field basis gave comparable data with regard to bacterial removal by sands (Orlob and Krone, 1956). Data presented in this report also indicate that both coarse-grained sands and fine-grained soils remove over 90 percent of bacteria from waste water but subsequent filtration of water tends to cause certain amount of desorption of the bacterial growth. Thus, all of the above studies suggest that soils or sands can filter out bacteria, but incompletely, and some pollution of ground water from infiltration of sewage probably occurs.

In a pilot study (Robeck and others, 1962-a) on the movement of coliform organisms through water-saturated sands containing ABS, it was concluded that:

(1) ABS at 1–10 ppm did not have a significant influence on the movement of coliform organisms through homogeneous sands.

(2) Coliform organisms traveled much more slowly than salt or ABS. They did not penetrate much beyond 6 feet in 417 days for water moving at 0.4 feet/day and

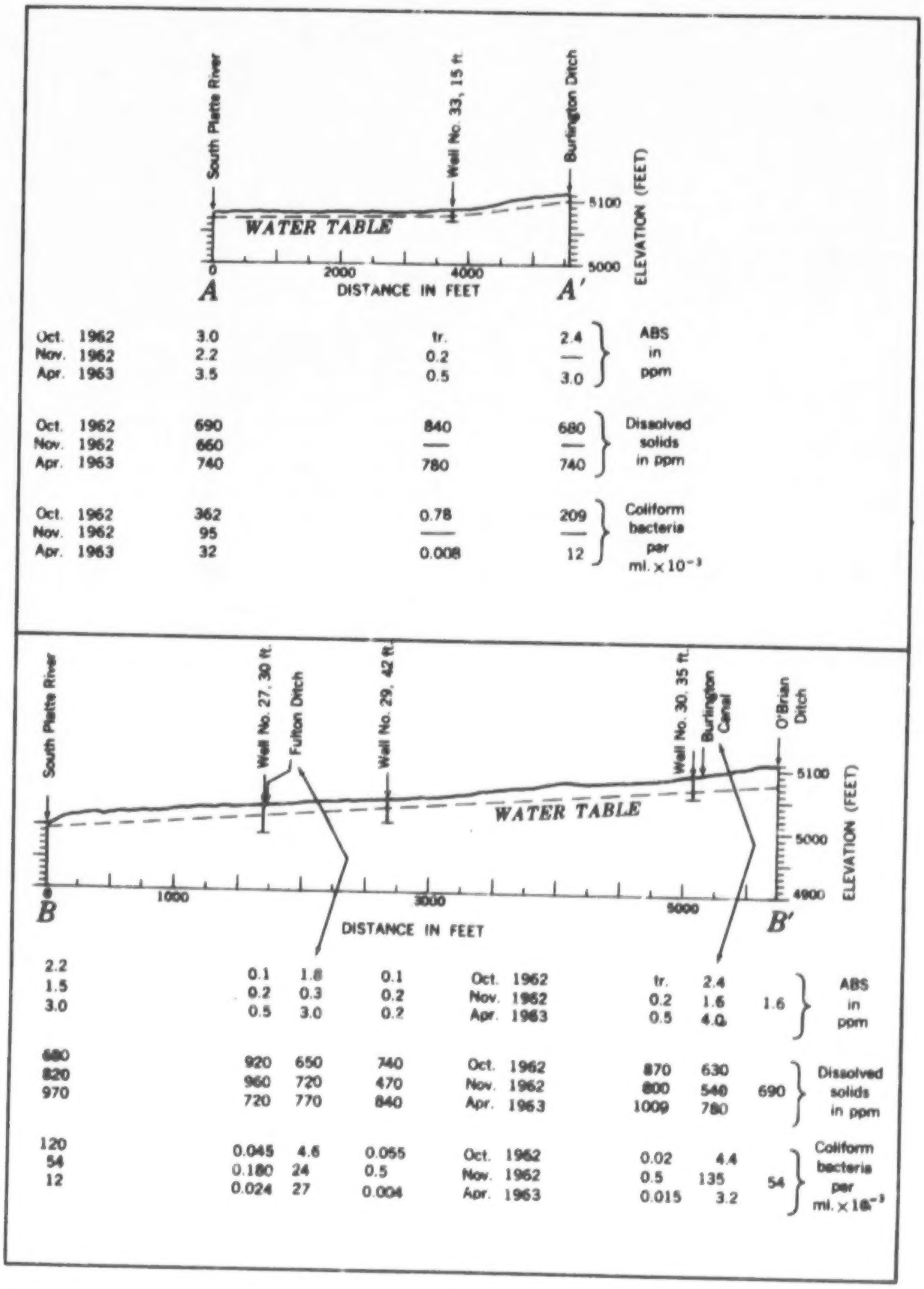
(3) Doubling the rate of water movement to 0.8 feet/day merely reduced the coliform arrival time at 4 feet from 114 days to 82 days.

However, the data reported on the pilot study above and that measured in the field are at variance. A study on ABS in Wisconsin ground water (Nichols and Koepp, 1961) showed that 32.1 percent of 2,167 wells tested were polluted with ABS; the authors indicated that as the concentration of ABS increases in ground water, the percentage of bacteriologically unsafe water becomes larger. Therefore, this field study suggests that some uncertainty exists between ABS and bacteria in ground water with regard to pollution of well water.

The only other field study somewhat similar to ours, as reported below, involved the natural infiltration of river water (Illinois River near Peoria) and from recharge pits into ground water wells nearby (Harmeson, 1961). At various sampling points on the Illinois River, ABS concentrations ranged from 0.22 to 0.96 ppm. In a ground water test well in close proximity to a recharge well using river water, ABS concentrations ranged from 0.09 to 0.51 ppm suggesting little removal by the soil from this infiltrating water. Further out (up to 1000 feet) from the river and recharge pits, ground water wells contained average amounts of ABS that ranged from 0.02 to 0.07 ppm. This study clearly demonstrated that polluted water (containing ABS) can infiltrate through soil into ground water, and that the distance between the source of pollution and its final destination is important to the removal of ABS by soil.

In our study the infiltration of ABS, coliform bacteria, and dissolved solids into ground water from irrigation ditches east of the South Platte River was determined. The location of the wells from which profiles (A-A, B-B, C-C, and D-D) were drawn are shown on figure 96. Figure 102 (in pocket) shows contours drawn to represent elevation of the ground water surface. The only salient features indicated on figure 102 are the steepnesses in gradients of the ground water table in parts of profiles B-B and C-C; this feature suggests that ground water would tend to move more rapidly through these areas than A-A or D-D other things being equal. Differences in transmissibility may also be the determining factor of these gradients.

Figure 103 shows the profiles of sections A-A and B-B with indicated changes of ABS,


South Platte River
Well No. 33, 15 ft.
Burlington Ditch
WATER TABLE
0
2000
4000
DISTANCE IN FEET
A
A′
5100
5000
ELEVATION (FEET)
South Platte River
Well No. 27, 30 ft.
Fulton Ditch
Well No. 29, 42 ft.
Well No. 30, 35 ft.
Burlington Canal
O'Brian Ditch
WATER TABLE
1000
3000
5000
B
B′
DISTANCE IN FEET
5100
5000
4900
ELEVATION (FEET)

Oct. 1962	3.0	tr.	2.4	ABS in ppm
Nov. 1962	2.2	0.2	—	
Apr. 1963	3.5	0.5	3.0	
Oct. 1962	690	840	680	Dissolved solids in ppm
Nov. 1962	660	—	—	
Apr. 1963	740	780	740	
Oct. 1962	362	0.78	209	Coliform bacteria per ml. × 10^{-3}
Nov. 1962	95	—	—	
Apr. 1963	32	0.008	12	

2.2	0.1	1.8	0.1	Oct. 1962	tr.	2.4		ABS in ppm
1.5	0.2	0.3	0.2	Nov. 1962	0.2	1.6	1.6	
3.0	0.5	3.0	0.2	Apr. 1963	0.5	4.0		
680	920	650	740	Oct. 1962	870	630		Dissolved solids in ppm
820	960	720	470	Nov. 1962	800	540	690	
970	720	770	840	Apr. 1963	1009	780		
120	0.045	4.6	0.055	Oct. 1962	0.02	4.4		Coliform bacteria per ml. × 10^{-3}
54	0.180	24	0.5	Nov. 1962	0.5	135	54	
12	0.024	27	0.004	Apr. 1963	0.015	3.2		

Figure 103.—Profiles of sections A-A and B-B showing indicated changes of ABS, dissolved solids, and coliform bacteria from infiltration.

dissolved solids, and coliform bacteria from infiltration. The data show that both ABS and coliform bacteria have infiltrated through fine-grained, sandy loam soil for a vertical distance of about 10 feet into the aquifer and have transferred nearly 2000 feet in direction of ground water flow to well No. 33; both of these constituents have been significantly filtered out by the Brighton sandy loam overlying the aquifer (composed of sandy alluvium and gravel) and the aquifer. Total dissolved solids seem to be little affected by infiltration, most likely because of variation of their filtration and subsequent leache-ability characteristics during infiltration. Another possible interpretation of the results is as follows: little or no removal of ABS and bacteria occurs by infiltration of the ditch water through the unsaturated zone; the apparent decrease in concentration of these constituents might be from dilution by ground water. No significance is to be attached to the change in ABS concentration in ground water with time because of limitations in the analytical method (Methylene Blue). However, it seems apparent that both ABS and coliform bacteria can migrate through fine-grained soils and aquifer sands for large distances without total removal.

Profile B-B (figure 103) shows concentration of various constituents in well No. 30 from infiltration attributed to sources of Burlington and O'Brain ditches; this well is located 200 feet and 1400 feet from these two ditches, respectively. As in the case for profile A-A, most removal of the pollutants seems to have occurred from downward percolation with little change in removal of pollutants taking place along horizontal flow through the aquifer. Little change in the dissolved solids content is similarly shown on this profile. It is further indicated that little removal of pollutant occurs within the aquifer as shown by similar concentration of pollutants in wells 29 and 30; well 29 is located about 5000 feet in direction of ground water flow from well 30. Well 27 shows pollution characteristics similar to those of well 30.

Figure 104 (in pocket) shows profiles of sections C-C and D-D with changes in concentrations of ABS, dissolved solids, and coliform bacteria from infiltration of ditch water through the Brighton sandy loam (vertically) into an alluvium aquifer (sandy gravel) with additional movement of water horizontally, or nearly so, along the aquifer into various wells. Most of the effects described for removal of the pollutants in profiles A-A and B-B also apply to profiles C-C and D-D. It is significant to indicate that wells that penetrate to depths of nearly 200 feet (well 23, profile C-C; and well 15, profile D-D) show pollution similar to the much shallower wells.

From the observations of the field infiltration of ABS, dissolved solids, and coliform bacteria of irrigation ditch water into ground water, the following conclusions can be made:

(1) ABS and coliform bacteria seem to be significantly reduced by infiltration through the unsaturated zone; dissolved solids do not seem to be removed in comparison to their concentration in the surface water and ground water. This inefficient removal of dissolved solids in the unsaturated zone may be attributed to adsorption on and subsequent leaching of these solutes from soils.

(2) Once a pollutant gets into ground water (saturated flow), little significant removal of ABS or dissolved solids, even for movement over extensive horizontal distances, is to be expected. This result is in agreement with the data shown for flow of sewage effluent through various soil columns (saturated flow).

(3) Flow of polluted water through unsaturated, fine-grained soils, does not permit removal of all pollutants such as ABS or coliform bacteria but may provide significant reduction in these constituents.

(4) It is also possible that soils do not significantly remove ABS and bacteria by downward infiltration of polluted water, but, that these constituents merely become diluted by ground water and reflect an apparent decrease in concentration between the source and well. It also seems plausible that a combination of (3) and (4) may operate in nature to reduce effects of pollution.

SUMMARY

This report indicates the prevalence of ABS as one form of pollution of both surface water and ground water. Data are given to support the premise that anionic surfactants dominate the synthetic detergent market with respect to production and usage; these data are significant because anionic surfactants, presently employed in detergents, definitely contribute to water pollution problems. Various ionic forms of surfactants are listed along with aspects of pollution attributed to ABS. The concentration of ABS in public water supplies, surface water, domestic raw sewage, sewage plant effluents, septic tank effluents, and ground water are listed as evidence of water pollution from incomplete biodegradation of branched-chain ABS.

Analytic techniques are described and reviewed in some detail for determination of anionic and nonionic surfactants in water. Techniques for determination of ABS are emphasized. The colorimetric procedure (Methylene Blue) is employed nearly universally for determination of ABS in natural water or waste water. Certain limitaions and precautions regarding use of this method are indicated; variables to be considered in use of the methylene blue method are:

(1) pH of extraction

(2) time of measurement of the colorimetric complex after extraction

(3) purity of methylene blue dye

(4) pre-extraction versus direct extraction and

(5) effect of pre-oxidation by chrome-sulfuric acid

It has been suggested that the precision of the method increases with decrease in concentration. Infrared spectrometry has been employed to give an unequivical identification of ABS. The method, however, is time consuming and involves expensive instrumentation, which has not permitted many analysts to use the technique on a routine basis. A new method for determination of ABS in terms of its sulfur content by neutron activation analysis is suggested. With certain refinements, this technique may possibly be adapted to orders of magnitude below concentrations of ABS presently determined with the methylene blue procedure. In addition to the above methods, anionic surfactants like ABS might be determined by paper chromatography, gas chromatography, salting-out chromatography, ion exchange, and ultraviolet spectrometry.

Methods for determination of nonionics in water are essentially unestablished. Because of the vast number of nonionic compounds, methodology for determination of specific compounds or reactive groups is still lacking. Methods involving volumetric, gravimetric, titration techniques, use of physical properties colorimetric and spectrophotometric procedures have been indicated. Techniques such as paper chromatography, nuclear magnetic resonance, and ion exchange have also been suggested.

Surfactants like ABS in solution may influence such properties as surface tension, critical micelle concentration, foaming, and dispersion and flocculation phenomena. Surface tension may alter properties at the air solution interface and solid-liquid interface which may contribute to foaming and adsorption on solids, respectively. The Gibbs adsorption equation was employed to calculate the amount of ABS adsorbed at the air-solution interface from surface tension measurements at various concentrations of ABS (2°C to 35°C). The ABS adsorption at the air-surface interface was then used to calculate the cross-sectional area of the ABS ion in solution. The cross-sectional area can be used to evaluate monolayer versus multilayer adsorption on solid surfaces. On sand grains dodecyl ABS is probably adsorbed as a monomolecular film. The completeness of surface coverage on sand decreases with increase in chain length of ABS between dodecyl ABS and hexadecyl ABS.

Surface tension of commercial surfactants was measured at 20°C using a Cassel tensiometer. For the concentrations (1 to 10 ppm) to be expected in natural water, predictable surface tension values from ABS alone in solution range from 65 to 72 dynes cm^{-1}. Between pH 3 and pH 10, surface tension of ABS solutions increases with increase in pH. The surface tension of sewage effluents may range from 45 to 71 dynes cm^{-1}. These lower surface tension values of natural water indicate that surfactants, other than ABS, are in solution and probably at much higher concentrations than ABS. A knowledge of the surface tension of water is important, especially in studies involving recharge operations or natural infiltration, as this parameter can influence the rate of movement through coarse-grained or fine-grained sediments.

Factors influencing the CMC in surfactant solutions are discussed with possible applications to adsorption on clay surfaces.

Certain problems created by foaming from ABS and other surfactants in solution are discussed. An apparatus is described for measurement of foaming characteristics of various surfactant solutions. Because ABS will not produce stable foams below about 2.0 ppm, vigorous foaming in natural water containing less ABS than this amount must be attributed to the surface activity of constituents in water in addition to ABS; these other constituents might be other surfactants discharged from sewage plants or from creation of "natural surfactants" in water from biological activity such as "saponin" from plants. Foams seem to be more stable at lower temperatures (10° C). Foaming from ABS occurs most readily in the pH range 7 to 10. Escherichia coli in water tends to enhance foaming, but small concentrations of cationic surfactants may reduce or destroy foams resulting from ABS.

A brief discussion of dispersion and flocculation phenomena is given. Measurements on the viscosity of surfactant solutions containing bacteria and clay in suspension were made with the aid of a Ubbelohde viscometer. Viscosity of solutions containing ABS and other surfactants in concentrations (1000 ppm) exceeding those in natural is about equivalent to that of normal water. Large concentrations of bacteria (100 million per ml) in solution give viscosities similar to that of water at a specified temperature. ABS and other detergent components on solution can influence the viscosity of clay suspensions along with pH, type of clay, and temperature and, therefore, contribute to dispersion-flocculation phenomena. If montmorillonite is in solution with surfactants, the viscosity of this suspension becomes as much as 25 times less mobile than similar water containing no solid. Thus, the flow of clay-water suspensions can be greatly altered by the presence of detergent components which may have a significant influence in many areas of fluid-flow studies such as open-channel flow and sedimentation, flow in pipes, under-ground flow through fractures and solution openings, and in drilling-mud technology.

Studies on the survival of pure cultures of Escherichia coli in water showed that ABS concentration, pH, temperature, and nutrients are important. Optimum survival in detergent solutions occurs at low temperature of water (less than 20° C), in neutral solution (pH of 7), and with phosphate, carboxymethylcellulose, and other constituents of commercial detergents in solution. In general, bacteria seem to disappear logarithmically with respect to time. Low concentrations of ABS (10 ppm or less) do not prolong growth any more than distilled water. High concentrations of ABS (100 to 1000 ppm) are toxic to coliform bacteria; the toxicity, which kills bacteria, probably is due to changes in permeability of the bacterial membrane which initiates or develops lysis.

Biodegradation of branched-chain and straight-chain ABS was studied using the river water die-away test. Branched-chain ABS cannot be significantly degraded under aerobic or anaerobic conditions. Straight-chain ABS can be nearly totally degraded in aerated water in 2 to 10 days, the amount of time decreasing with increase in temperature and probably depending somewhat on bacterial concentration. Under anaerobic conditions straight-chain ABS is not significantly degraded. Thus, the use of newer types of straight-chain ABS in detergent formulations should tremendously improve water pollution problems in sewage plants and surface waters but ground water pollution (under anaerobic conditions) from their use, to some extent, is to be anticipated.

The adsorption of branched-chain ABS on various clays, hydroxides, soils, and synthetic materials was studied by a combined radiochemical-dialysis technique. Most natural materials are inefficient adsorbents for ABS in comparison to synthetic adsorbents such as "Baymal" (colloidal alumina) and activated charcoal. The ability of natural materials to remove ABS is complex and depends upon:

(1) concentration of ABS in solution

(2) length of the alkyl chain (number of carbon atoms)

(3) pH of the solution

(4) in some instances having phosphate in solution, especially for clays

(5) type and amount of ionized salt in solution and

(6) organic content of the adsorbent.

In filtering of ABS from acid waste solutions, goethite [$Fe(OH)_3$] and gibbsite [$Al(OH)_3$] seem to possess desirable properties. The inefficient removal of ABS by most natural materials alludes to a partial explanation of ground water pollution from this constituent.

The filtration of ABS, bacteria, and dissolved solids from a primary sewage effluent by various natural materials was studied for conditions of saturated flow. The following conclusions were made:

(1) Most soils removed over 90 percent of the bacteria from sewage within a few feet of travel which contributed to severe clogging in the finer-grained soils. With some soils, bacteria seem to be desorbed with amount of volume throughput; ABS and other constituents attached to such slimes would also be desorbed.

(2) ABS can be removed significantly with initial infiltrating effluent but the amount decreases with increased amount of solution throughput. Ottawa Sand and sandy loam showed little tendency to remove ABS but some of the less common soils were effective ABS filters such as muck, weathered-basalt, and greensand-marl.

(3) Dissolved solids moved through the columns virtually unaffected with respect to removal.

(4) In general, the criteria used to account for adsorption of ABS on minerals can be applied also to soils but additional hydraulic and bacteriological factors also influence ABS removal for saturated flow.

The pollution of a large river (South Platte) from the discharge of a primary sewage effluent (80 to 100 million gallons per day) indicated that severe changes in concentration of certain constituents is to be expected and maintained for considerable distance of flow without significant dilution. Over a period of about 18 months, the following changes were observed in the river about one mile from the discharge point:

(1) streamflow, 310 to 360 cfs (increase)

(2) ABS, 0.7 to 1.8 ppm (increase)

(3) total bacteria, 120,000 to 375,000 per ml (increase)

(4) coliform bacteria, 1,000 to 25,000 per ml (increase)

(5) biological oxygen demand, 6 to 90 ppm (increase)

(6) dissolved solids, 430 to 550 ppm (increase)

(7) dissolved oxygen, 7 to 3.5 ppm (decrease)

Most of the above constituents were maintained for an additional 24 miles of river flow without significant change. Thus, the discharge of sewage plant effluents into rivers can create serious deterioration of water quality. Such constituents are important to a water quality network study and should be monitored along with other chemical and biological species. The evaluation of such parameters are a necessity in determining the feasibility of using such water as a municipal supply or for studies regarding the infiltration (recharge) or river water into the ground.

Infiltration studies of polluted river water from diverted irrigation ditches through sandy loam into an aquifer consisting of alluvium (sand and gravel) indicated the following:

(1) ABS and coliform bacteria are significantly reduced by infiltration through the unsaturated zone; dissolved solids do not seem to be removed in comparison to their concentration in surface water. This inefficient removal of dissolved solids in the adsorption on and subsequent leaching of these solutes from soils by the infiltrating water.

(2) Once a pollutant gets into ground water (saturated flow) little additional change in removal of ABS or dissolved solids, even for movement over extensive horizontal distances, is to be expected. This result is in agreement with the data shown for flow of sewage effluent through various soil columns (saturated flow).

(3) Flow of polluted water through unsaturated, fine-grained soils does not permit total removal of contained pollutants, ABS and coliform bacteria, but may provide significant reduction in these constituents.

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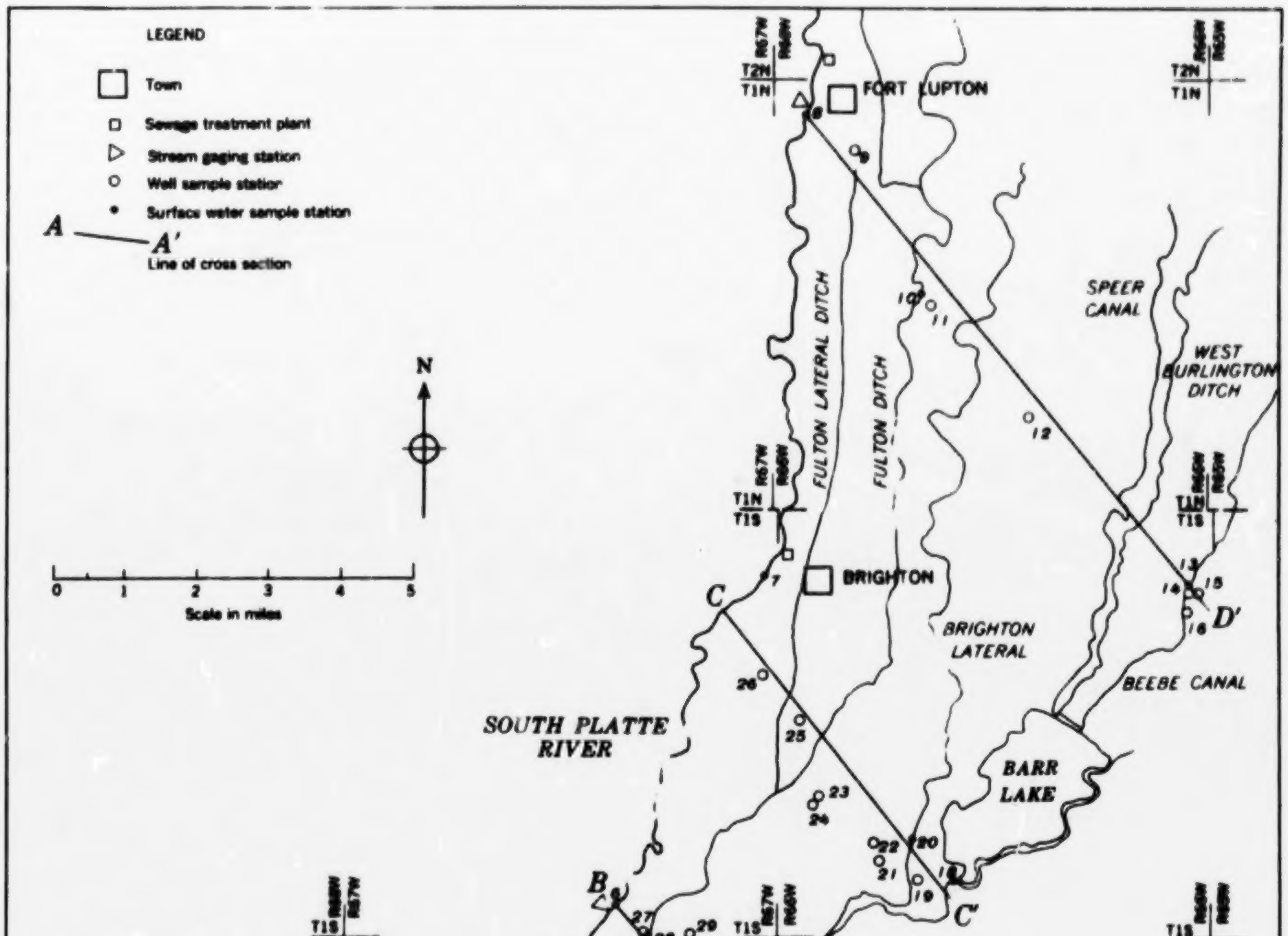
LEGEND
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THORNTON
DENVER
SOUTH PLATTE RIVER
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BEEBE CANAL
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O'BRIAN CANAL
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FIGURE 96.–MAP SHOWING LOCATION OF AREA STUDIED AND SAMPLING POINTS FOR SURFACE WATER AND GROUND WATER.

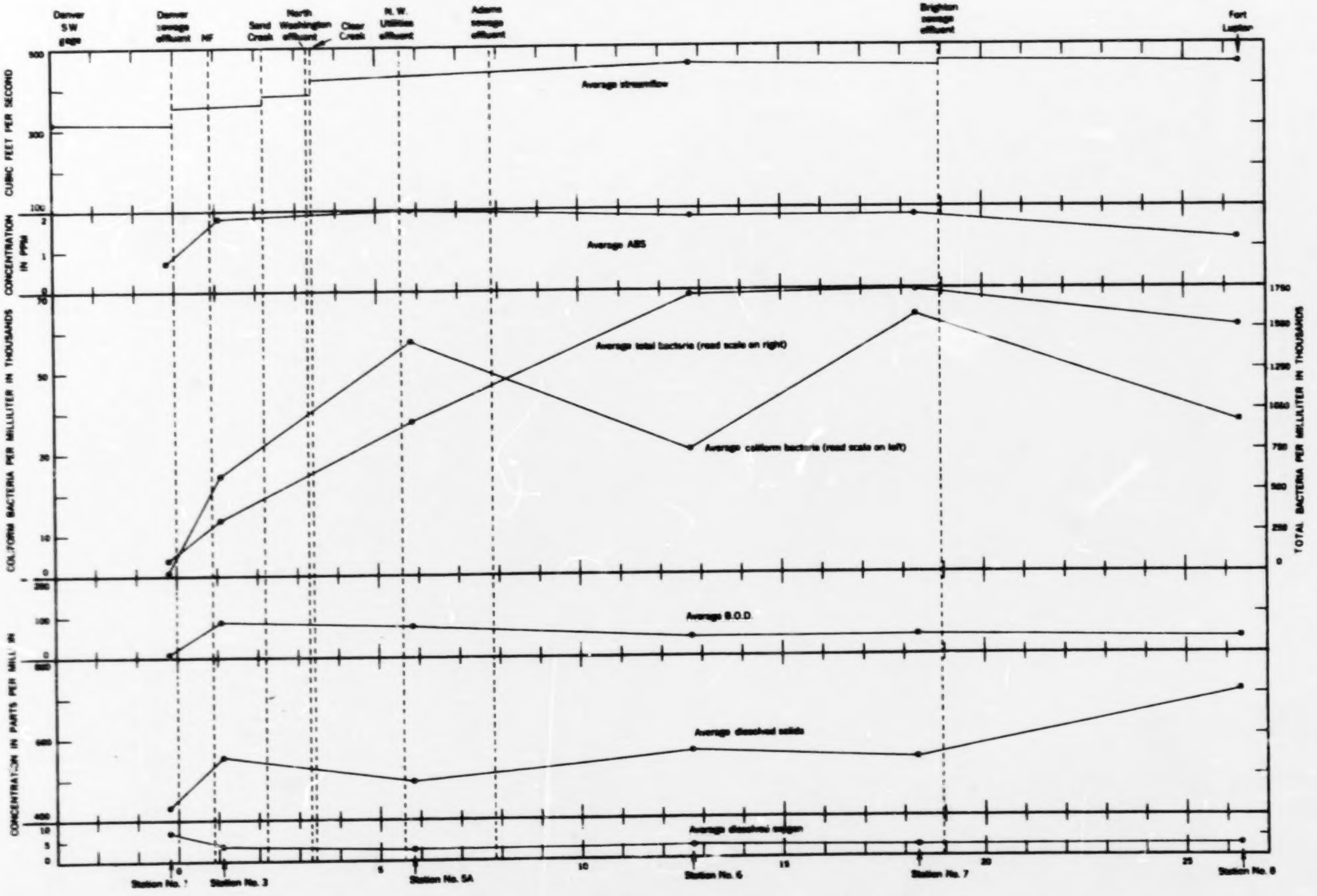


FIGURE 97.–CHANGE IN AVERAGE CONCENTRATION OF SELECTED CONSTITUENTS IN SOUTH PLATTE RIVER WITH RESPECT FROM DENVER TREATMENT PLANT FOR 1962.

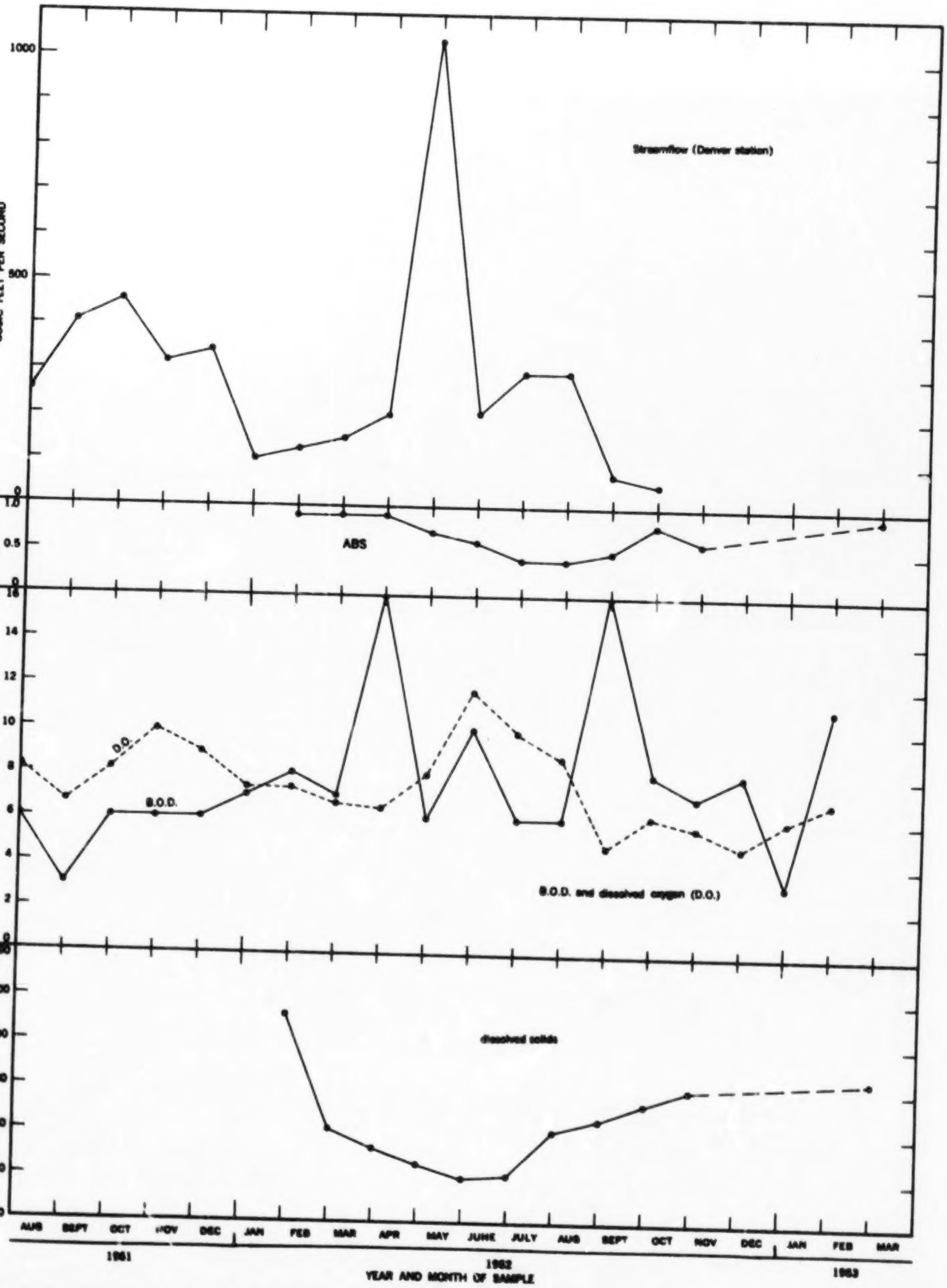


FIGURE 98.—VARIATION OF STREAMFLOW, ABS, D.O., B.O.D., AND DISSOLVED SOLIDS 0.2 MILES ABOVE DISCHARGE POINT OF DENVER SEWAGE EFFLUENT FROM JULY, 1961, TO FEBRUARY, 1963.

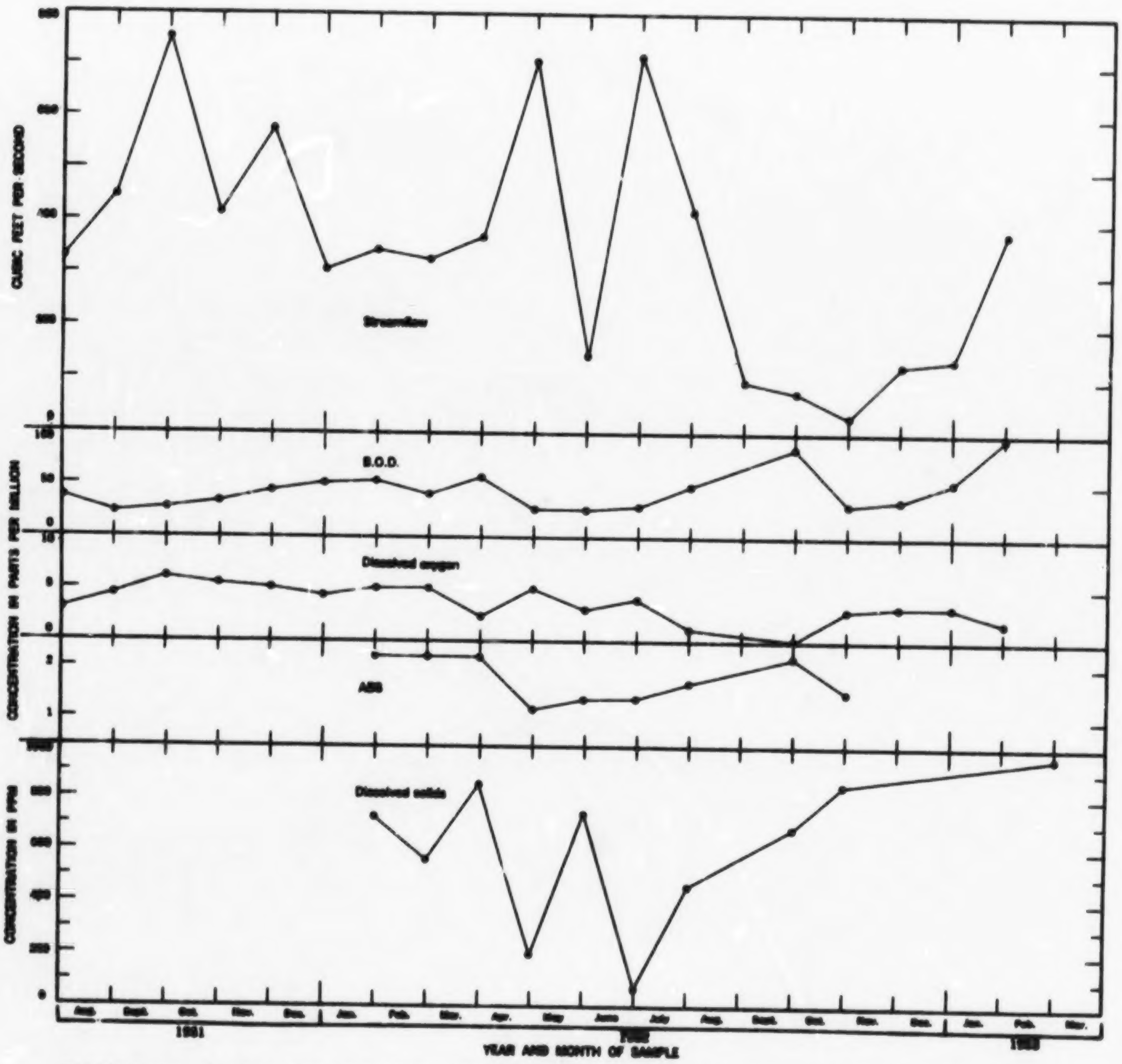


FIGURE 100.—VARIATION OF STREAMFLOW, ABS, D.O., B.O.D., AND DISSOLVED SOLIDS 12.75 MILES BELOW DISCHARGE POINT OF DENVER SEWAGE EFFLUENT FROM JULY, 1961, TO FEBRUARY, 1963.

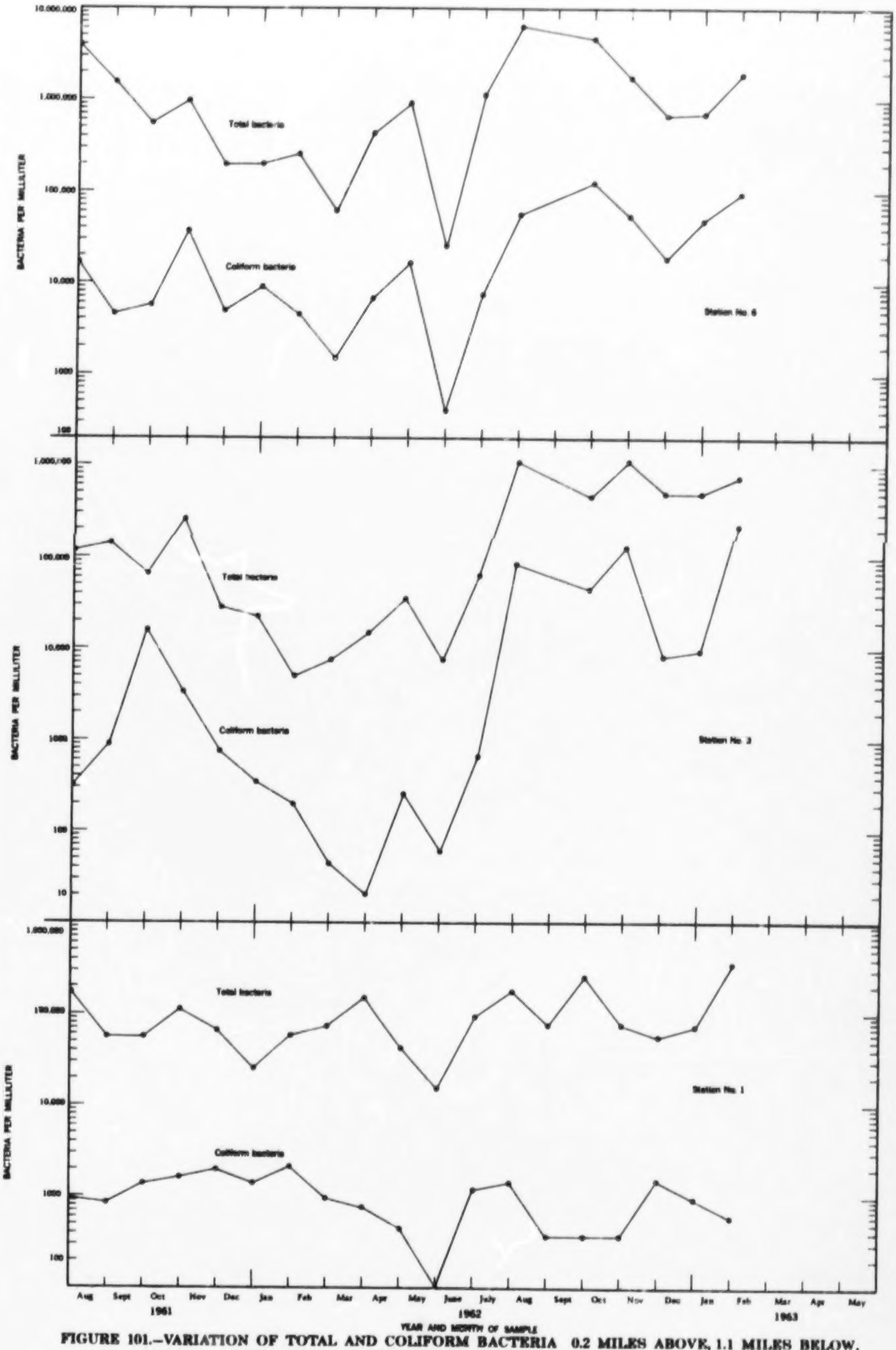


FIGURE 101.–VARIATION OF TOTAL AND COLIFORM BACTERIA 0.2 MILES ABOVE, 1.1 MILES BELOW, AND 12.75 MILES BELOW DISCHARGE POINT OF DENVER SEWAGE EFFLUENT.

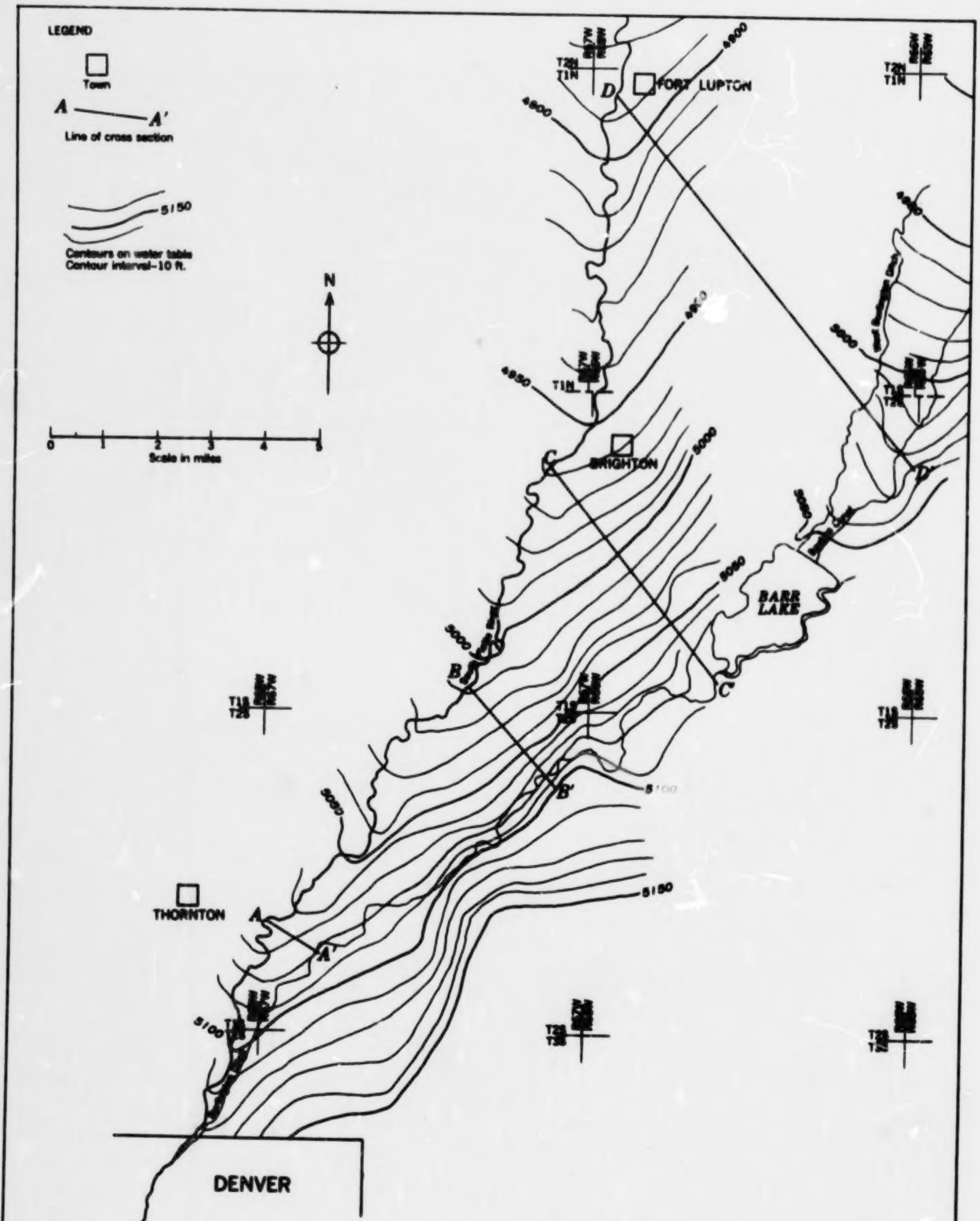

LEGEND
Town
A — A'
Line of cross section
5150
Contours on water table
Contour interval–10 ft.
N
0 1 2 3 4 5
Scale in miles
T2N
T1N
FORT LUPTON
D
4900
4850
T1N
BRIGHTON
C
5000
5050
BARR LAKE
C'
D'
B
B'
T1S
T2S
5100
5150
THORNTON
A
A'
DENVER

FIGURE 102.–CONTOURS SHOWING THE ELEVATION OF THE GROUND WATER SURFACE.

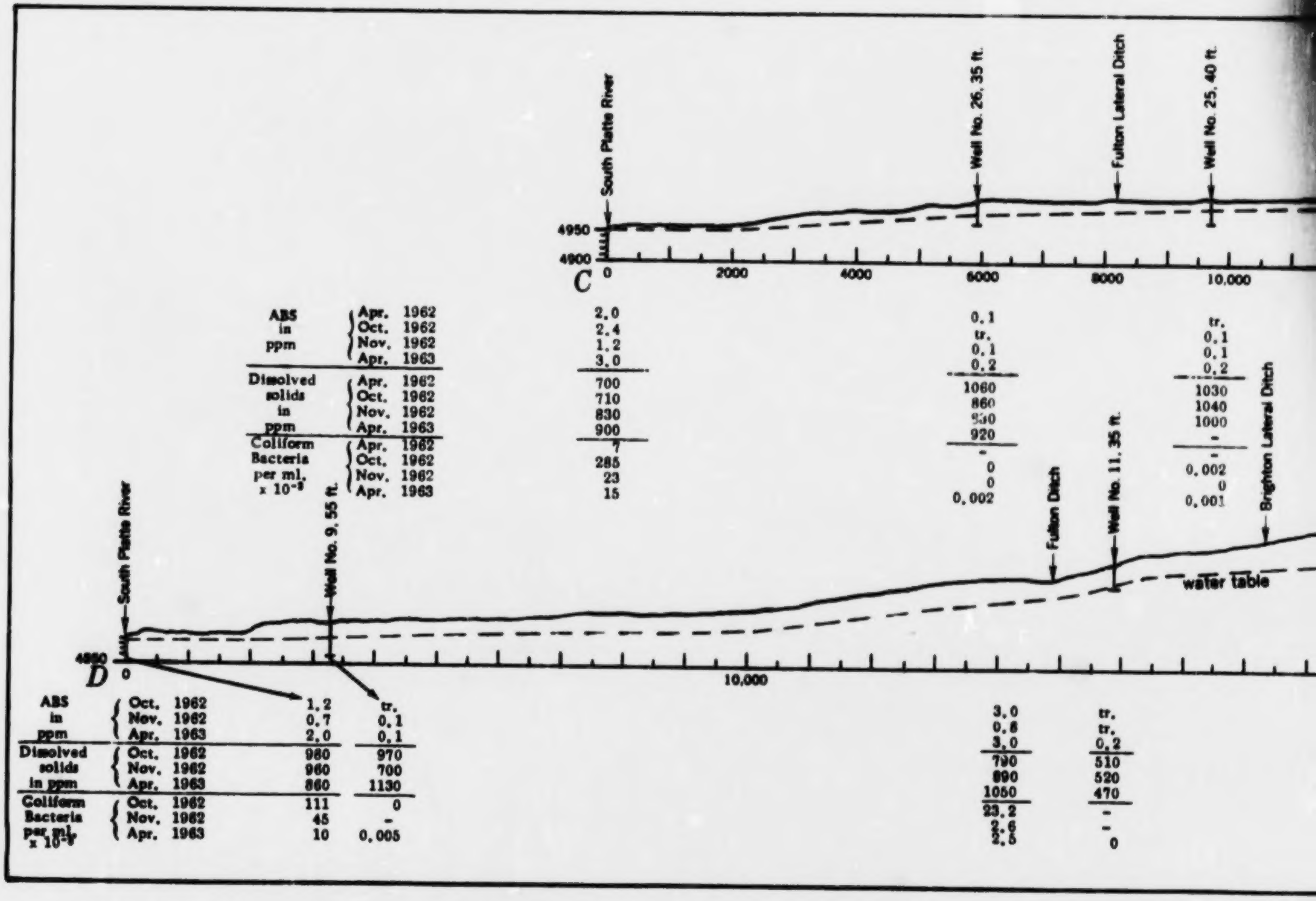
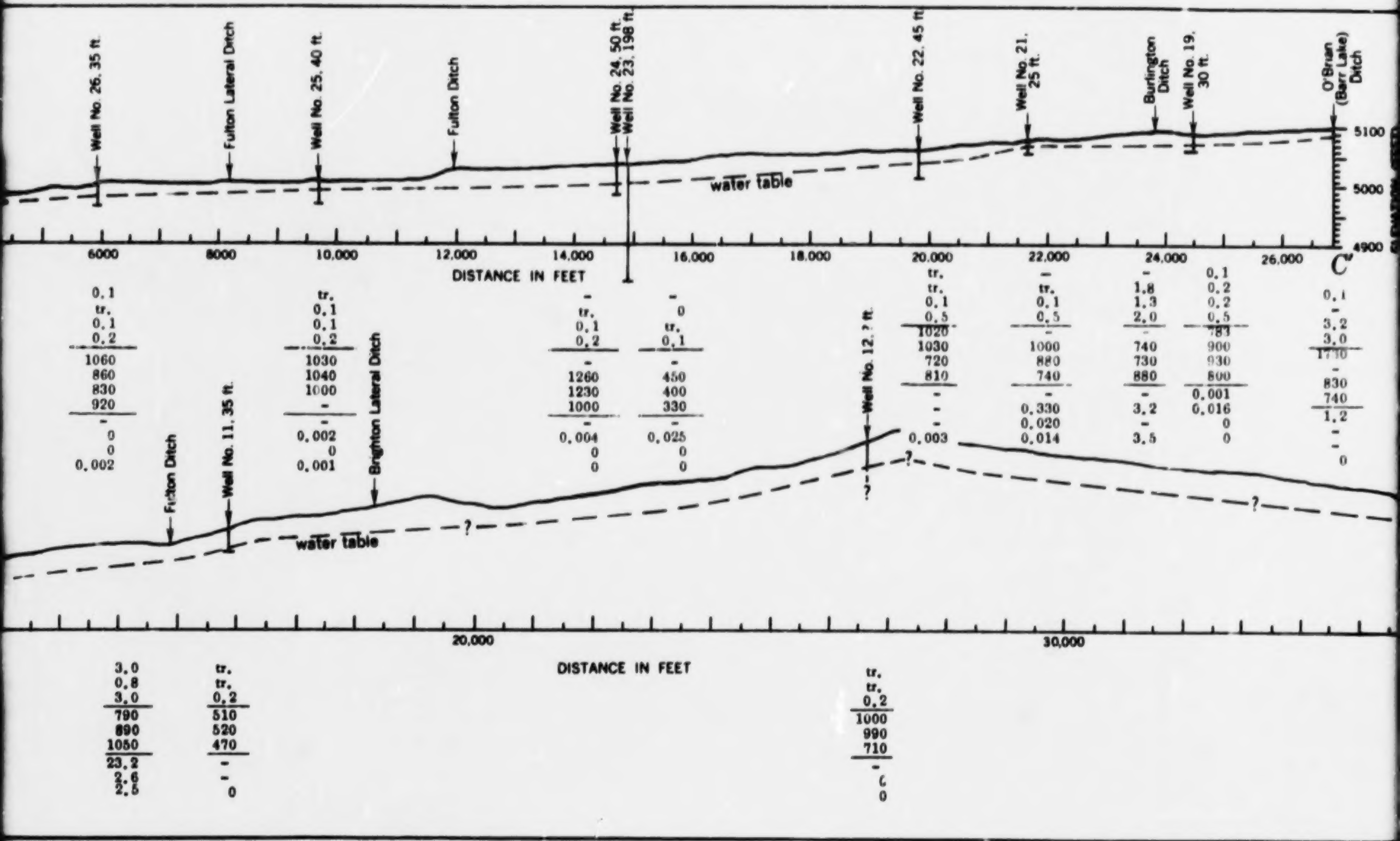


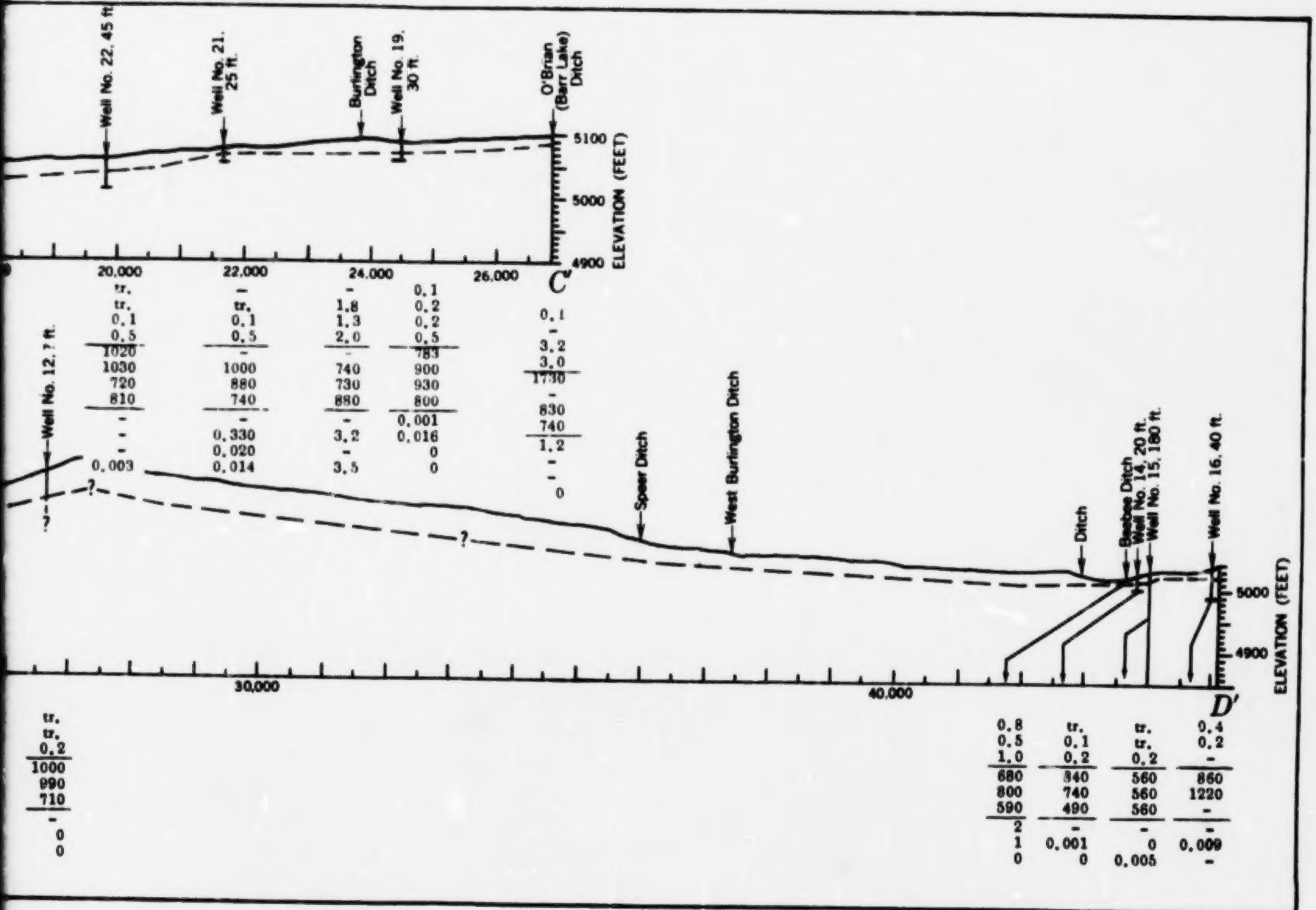
FIGURE 104.--PROFILES OF SECTIONS C-C' AND D-D' SHOWING INDICATED CI

A


Well No. 26, 35 ft.
Fulton Lateral Ditch
Well No. 25, 40 ft.
Fulton Ditch
Well No. 24, 50 ft.
Well No. 23, 198 ft.
Well No. 22, 45 ft.
Well No. 21, 25 ft.
Burlington Ditch
Well No. 19, 30 ft.
O'Brian (Barr Lake) Ditch
water table
5100
5000
4900
6000
8000
10,000
12,000
14,000
16,000
18,000
20,000
22,000
24,000
26,000
DISTANCE IN FEET
C'
0.1
tr.
0.1
0.2
1060
860
830
920
-
0
0
0.002
tr.
0.1
0.1
0.2
1030
1040
1000
-
0.002
0
0.001
-
tr.
0.1
0.2
-
1260
1230
1000
-
0.004
0
0
-
0
tr.
0.1
-
450
400
330
-
0.025
0
0
tr.
tr.
0.1
0.5
1020
1030
720
810
-
-
-
0.003
-
tr.
0.1
0.5
-
1000
880
740
-
0.330
0.020
0.014
-
1.8
1.3
2.0
-
740
730
880
-
3.2
-
3.5
0.1
0.2
0.2
0.5
783
900
930
800
0.001
0.016
0
0
0.1
-
3.2
3.0
1730
-
830
740
1.2
-
-
0
Fulton Ditch
Well No. 11, 35 ft.
Brighton Lateral Ditch
Well No. 12, ? ft.
water table
?
20,000
30,000
DISTANCE IN FEET
3.0
0.8
3.0
790
890
1050
23.2
2.6
2.5
tr.
tr.
0.2
510
520
470
-
-
0
tr.
tr.
0.2
1000
990
710
-
0
0

D D-D' SHOWING INDICATED CHANGES OF ABS, DISSOLVED SOLIDS, AND COLIFORM BACTERIA FROM IN

B


Well No. 22, 45 ft.
Well No. 21, 25 ft.
Burlington Ditch
Well No. 19, 30 ft.
O'Brian (Barr Lake) Ditch
5100
5000
4900
ELEVATION (FEET)
20,000
22,000
24,000
26,000
C'
tr.
tr.
0.1
0.5
1020
1030
720
810
-
-
-
0.003
-
tr.
0.1
0.5
-
1000
880
740
-
0.330
0.020
0.014
-
1.8
1.3
2.0
-
740
730
880
-
3.2
-
3.5
0.1
0.2
0.2
0.5
783
900
930
800
0.001
0.016
0
0
0.1
-
3.2
3.0
1730
-
830
740
1.2
-
-
0
Well No. 12, ? ft.
?
?
?
Speer Ditch
West Burlington Ditch
Ditch
Beebee Ditch
Well No. 14, 20 ft.
Well No. 15, 180 ft.
Well No. 16, 40 ft.
5000
4900
ELEVATION (FEET)
30,000
40,000
D'
tr.
tr.
0.2
1000
990
710
-
0
0
0.8
0.5
1.0
680
800
590
2
1
0
tr.
0.1
0.2
840
740
490
-
0.001
0
tr.
tr.
0.2
560
560
560
-
0
0.005
0.4
0.2
-
860
1220
-
-
0.009
-

OLIDS, AND COLIFORM BACTERIA FROM INFILTRATION OF DITCH WATER.

C